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WALL-ROCK MINERALIZATION ALONG ONTARIO GOLD DEPOSITS.

GEORGE W. BAIN.

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SUMMARY.

This paper is a condensed summary of a series of studies on wall rock mineralization along gold lodes, especially those of northern Ontario. The gold deposits of Ontario are of three types. One type of deposit has a group of narrow quartz stringers in schistose rock in a zone of mining width and is typified by the Pearl Lake deposit. A second type of deposit occurs in a brecciated zone in intrusive rock and is illustrated by the Kirkland Lake lode. A third uncommon type has abundant tourmaline but is omitted entirely from this presentation. Wall rock mineralization along high grade parts of each type of deposit is described in detail and the features contrasted with those along low grade stretches. Differences between high and low grade are shown to be sufficiently distinctive to classify the grade of a mineralized zone into limited value groups by samples sufficiently large to make a microscope slide. This sample is representative for an average of about fifty feet in any direction along the McIntyre veins at Pearl Lake and the Teck Hughes section of the Kirkland Lake lode. Criteria developed should prove useful in interpreting diamond drill cores of veins as yet unseen.

INTRODUCTION.

WALL-ROCK mineralization along high grade [1] gold lodes of northern Ontario and Quebec differs from that along low grade deposits. This association of mineralization features with ore grade should increase the value of preliminary exploration of gold deposits. Lack of faith in preliminary exploration results dates back to the first deep diamond drill test in Ontario gold

[1] "Grade" is used throughout this paper to indicate relative gold content.

deposits made sometime previous to 1914. The drill passed beneath the Central and Main shafts of the Hollinger Mine and assays of the core indicated low grade and nonproductive lodes.[2] Development work showed that the core was not representative. In later years drillers learned to improve the results of their tests by saving the sludge as well as the core. But mine sampling experience indicates clearly that a channel the width of a drill core is not representative and that the gold values in a vein vary from foot to foot. Recently geologists have attempted to check the core assays by structure of specimens of the lode penetrated and represented by the core. The following study indicates that mineralization structures in the wall rock are a much better indication of the representative or non-representative value of the core assay than is the structure of the quartz vein. The following paper outlines the principal structures indicative of values and presents a possible genetic relation between wall rock mineralization and the gold content of the adjacent lode.

Wall-rock mineralization was studied in representative gold-producing areas of northern Ontario and Quebec such as the Howey deposit at Red Lake, the McIntyre at Pearl Lake, the Teck Hughes at Kirkland Lake, and the Siscoe and some small vein systems in Quebec. Pearl Lake and Kirkland Lake deposits received most detailed study because each is an outstanding example of the two types of deposit in the Canadian Shield. Each Pearl Lake gold lode is a group of quartz stringers in a sheared or schistose zone in Keewatin volcanics. The Kirkland Lake deposit is in a fault zone and branching fissures in brittle, massive augite syenite, syenite porphyry, and quartz porphyry. Mineralization in fissile, schistose rocks of the Pearl Lake district differs greatly from that in the massive fractured rocks at Kirkland Lake. Both types of deposit are encountered in the Siscoe deposit and the Howey mine.

Reports of the Geological Survey of Canada,[3] the Ontario

[2] Cole, A. A.: Ann. Rept. T. & N. O. Ry. Comm., Mining engineer's report for 1914, p. 15, 1915.

[3] Cooke, H. C., James, W. F., and Mawdsley, J. B.: Geology and Ore Deposits of Rouyn-Harricanaw Region, Quebec. Can. Geol. Surv., Mem. 166.

Bureau of Mines,[4] the Quebec Bureau of Mines,[5] and of geologists and engineers in the employ of mining companies,[6] give descriptions of these deposits but deal mainly with the major relationships of the veins rather than with recognition of specific attributes of high grade varieties of them.

Purpose of Investigation.

Extensive carbonatization is the most impressive change noted in gold deposits in northern Canada; pyritization, silicification and chloritization receive mention. The specific purpose of this investigation was to find associated with these changes some feature or group of features occurring along high grade veins or high grade sections of veins and absent along low grade, nonproductive, or barren stretches. The motive of the work is to increase effectiveness of diamond drilling and field examination of prospects and to prevent abandonment of known lodes because of inadequate exploration, rather than to help find new areas of mineralization.

Scope of Investigation.

The investigation was broader in number of districts visited, number of veins and localities examined and number of sections studied on any specific vein than the following descriptions indicate. Descriptions do not indicate the grade of ore for an entire mine, nor variation of grade of ore with horizontal or vertical extension for more than fifty feet from the specimen; they are specific examples to show the value of the criterion developed.

Great vertical range of deposits open for study at Pearl Lake makes it especially useful. Development methods at Kirkland

[4] Burrows, A. G.: Porcupine Gold Area. Ont. Bur. Mines, Ann. Rept., vol. 33, pt. 2, pp. 1–84, 1924. Todd, E. W.: Kirkland Lake Gold Area. Ont. Bur. Mines, Ann. Rept., vol. 37, pt. 2, pp. 1–176, 1928.

[5] Bancroft, J. A.: Kienwisik Gold Area. Dept. of Colonization, Rept. of Mining Operations in Quebec for 1912.

[6] Robinson, H. S.: Geology of Pearl Lake Area. ECON. GEOL., vol. 18, pp. 753–771. Bain, G. W.: Geology and Mineral Deposits of the Harricana and Bell River Basins. Bull. Can. Inst. Min. and Met., pp. 728–743, 1925. Graton, L. C., McKinstry, H. C., *et al:* Outstanding features of Hollinger Geology. Bull. Can. Inst. Min. and Met., pp. 1–20, 1933.

Lake leave a much narrower vertical range open to investigation at one time; but wall rock alteration in the levels of 1924 and 1927 is identical with that in present workings. Red Lake is a newly developed camp.

Metamorphism of the walls of lodes is divided into stages, since the same mineral commonly appears in two periods separated by important structural events. Influence of originally different rocks upon wall rock mineralization becomes significant where difference in chemical composition induces differences in physical behavior and ease of replacement at times when the rocks were subjected to stress; physical causes may appear to be chemical because of immediate associations. But under different associations, rocks chemically the same react differently under stress, and results appear to conflict with those seen elsewhere. Analysis of result, and cause and time of occurrence in a sequence becomes extremely important, and association of types, although reliable in a majority of cases, masks the actual influence.

Principal Distinctions Between High and Low Grade Mineralization.

The difference in the type of weakness in the wall rock at Pearl Lake from that at Kirkland Lake has great influence upon the distribution of the mineralization. Except for differences due directly to type of rock, the deposits show none of significance. Furthermore, significant distinctions between mineralization along high grade and along low grade lodes are related to a late stage introduction of chlorite, quartz and carbonate and recrystallization of coarse sericite. Chlorite favors the wider openings or potential openings and sericite and carbonate are deposited in the minutest ones. Metallic minerals such as galena, chalcopyrite and gold are associated with this mineralization at Pearl Lake (Fig. 1) and altaite, sylvanite, and gold accompany it at Kirkland Lake (Fig. 2).

Pearl Lake Type of Mineralization.—The significant mineralization at Pearl Lake occurs as columnar fringes made by filling of openings as they opened about pyrite (Fig. 3). The fringes

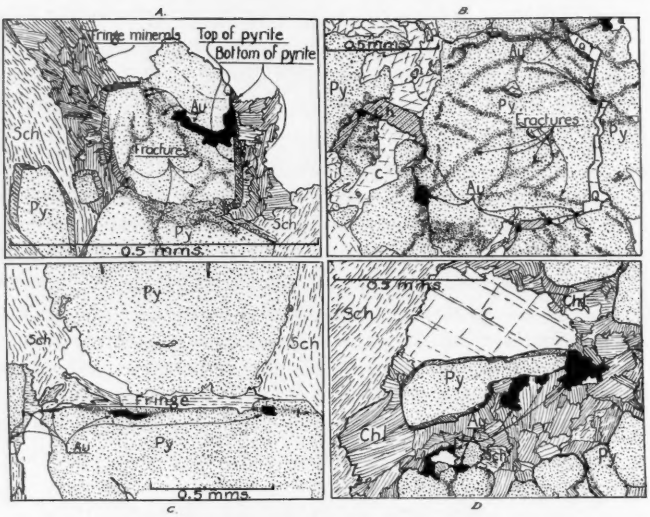

FIG. 1. Drawings to show chief modes of occurrence of gold in mineralized wall rock at Pearl Lake. Gold (*Au*, black), pyrite (*Py* stippled), chalcopyrite (*Ch*, stippled and lined), carbonate (*C*), chlorite (*Chl*), quartz (*Q*), and schist (*Sch*).

a. Gold in fissure in pyrite; wall of No. 7 vein, 1875 level. The gold filled fissure dips towards the top of the figure. Walls do not match because complementary parts are concealed inside the opaque minerals and show on the edge of the pyrite only. This single fissure frays out into fracture zones.

b. Gold and fringe minerals in a fissure in pyrite, walls of No. 13 vein, 3625 level. Gold, chalcopyrite, quartz and chlorite alternate as a filling of an almost vertical fissure on the lower right. Gold and chalcopyrite on the left fill flatly dipping fissures and replacement enlargements of them.

c. Gold in replacements along fractures near the edge of pyrite; walls of No. 5 vein, 200 level.

d. Gold and fringe minerals surrounding pyrite; walls of No. 13 vein, 3625 level. Fringe minerals and gold seem to have been deposited contemporaneously about pyrite.

are enlarged by replacement of the surrounding rock. Less commonly this columnar mineralization occupies fissures in pyrite. This mineralization occurs on all sides of the pyrite along high grade lodes and the fringes of introduced minerals are symmetrical about an axis of rotation through the pyrite; this structure is referred to hereafter as the rotational type (Fig. 4-*a*). Pyrite

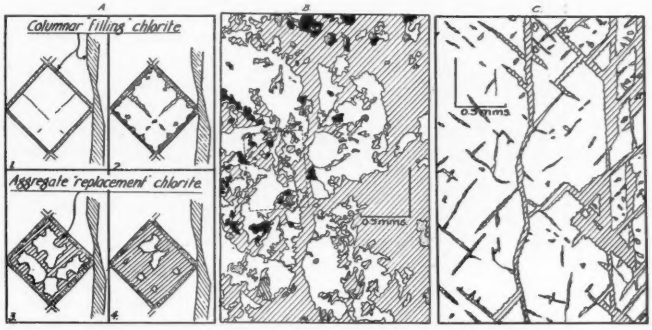

FIG. 2. Drawings to show alteration replacement of syenite at Kirkland Lake. Gold (black), tellurides (stippled), chlorite and carbonate (cross lined), and syenite (white).

a. Diagram showing progressive replacement outwards from a fracture system. Note the angular form and linear alignment of unreplaced minerals in the final stage.

b. Drawing of the green syenite to show intense chloritization and the association of gold and tellurides with chloritized walls of the fractures. (The area inside the dotted rectangle is a "negative or inverted" drawing of Fig. 7-*d*.)

c. Drawing to show the fracture pattern of "*b*." This represents the appearance of the rock when replacement was less complete, and is a frequent type in less mineralized sections.

along low grade lodes lacks these fringes or has them distributed symmetrically about a plane through the pyrite; this type of structure is referred to hereafter as the compressional type (Fig. 4-*b*). The rotational type of structure indicates opening of the rock to mineralization in all three space directions; by contrast, the compressional type of structure indicates opening in one or two direc-

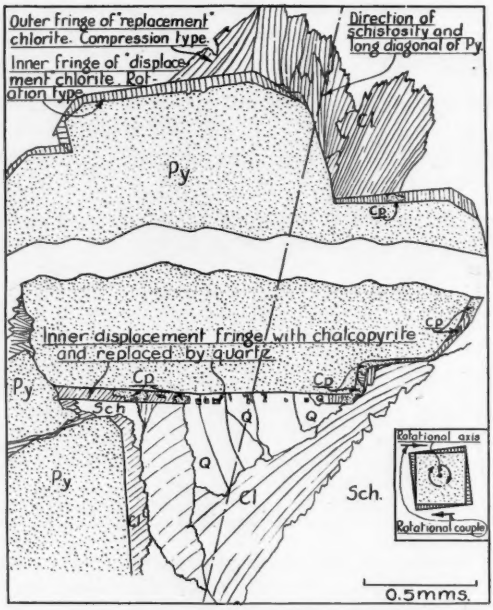

FIG. 3. Drawing of a pyrite metacryst in the pyritic schist section of No. 13 vein, 3625 level. It shows both replacement and displacement fringes. (The middle part of the metacryst between the broken lines shows no critical features and is omitted.)

Pyrite (*Py*, stippled) is separated from schist (*Sch*) along schistosity by a chlorite (*Cl*) fringe of combined replacement and displacement origin. (Compare Fig. 4-*b*.) This fringe is separated from pyrite by an inner displacement fringe of chlorite and chalcopyrite (*Cp*, stippled), which consists of wedges symmetrical about an axis of rotation through the pyrite (see inset). These rotational displacement fringes have matched walls and are the only type of diagnostic value in identifying high grade lodes. Both outer fringe and inner displacement fringe are replaced by quartz (*Q*) along the lower side of the pyrite. Note that the limit of the displacement fringe in the replacement zone is marked by straight edged chlorite residuals which wedge out towards the pyrite. Other chlorite residuals wedge out from a pyrite base. This replacement pattern is considered to indicate that the replacing solutions entered along the margins of the displacement fringe and attacked it from both sides. Con-

tions only. This mineralization is contemporaneous with the introduction of gold and the association of values with type of mineralization is due to this time relationship.

Kirkland Lake Type of Mineralization.—The significant mineralization at Kirkland Lake occurs as a filling of fissures and replacement enlargement of the fissures in brittle rock by columnar and aggregate chlorite and carbonate. Amount of replacement of fractured wall rock, especially by chlorite, is proportional to the gold content of the adjacent lode. Ratio of extent of replacement to gold values varies for each type of rock but is moderately constant for any specific type. As in the Pearl Lake type of deposit, freedom to mineralization by the chlorite-depositing solutions measures degree of mineralization by gold-depositing solutions. It should be recalled, however, that where the fringes are outside a district in which gold mineralization has occurred they are of no significance; the " favorable fringes " do not indicate gold; they indicate comparative ease of mineralization.

Acknowledgments.

The author wishes at this point to acknowledge assistance so that its importance, and the generosity with which it was rendered, will be fully realized. Privilege of examining underground workings and information on the relative values of different parts of veins in the McIntyre mine is due to the co-operation of R. J. Ennis. S. A. Wookey and John Beattie furnished information based upon experience gained from long association with the deposit, and H. S. Robinson supplied a most helpful analysis of data already available.

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temporaneous age of chlorite and chalcopyrite in the displacement fringe and of chalcopyrite and gold in fractures in pyrite (Fig. 1) shows that the important phase of gold mineralization accompanied progressive opening about pyrite to allow deposition of the displacement fringe. Quartz is later than the gold mineralization in this instance and seems to support Graton's thesis of the origin of the quartz veins. (See also Fig. 4-*a*.) However, on other evidence the author regards the main body of the quartz in the veins in the McIntyre mine to be earlier than these replacement fringes.

Equally important information on intermediate and deep levels at Kirkland Lake was made available to the author by D. L. H. Forbes. R. J. Henry supplied many significant observations made in mining development and exploration in the Teck Hughes part of the Kirkland Lake fault zone.

Professor L. C. Graton made many helpful suggestions. The replacement mode of emplacement of the fringes about pyrite receives emphasis as a result of conferences with Professor Graton during 1932.

WALL-ROCK MINERALIZATION AT PEARL LAKE, ONTARIO.

The Pearl Lake area of the Porcupine district is one of the two great gold producing regions in Canada; it is located at the end of a branch of the Temiskaming and Northern Ontario Railway from Porquis Junction. Gold is in quartz veins and pyritic schists and is recovered by cyanidation. The entire district produced during 1931 3,078,609 tons having a value of $19,891,521, or an average content of $6.48 per ton. (Approximately 18.3 per cent. averaging about $5.81 per ton came from the Dome mine, which is the only producer in the Porcupine district outside the Pearl Lake area.) Ore below $5 is considered low grade for this camp, whereas that above $10 is classed as medium or rich.

General Surroundings of the Veins.

Pearl Lake veins occur along shear zones cutting schistose volcanics, interstratified graywackes, and intrusive quartz porphyry. The volcanics are the most favorable wall rock, and highly silicified and albitized zones adjacent to the quartz porphyry are least promising. Chloritized and epidotized rocks predominate in the volcanic series and have sericite alteration superimposed upon this early metamorphism. Tuff and flow top fragments show mechanical elongation and alteration of the ferromagnesian minerals. The quartz porphyry is less deformed than the enclosing schist but the quartz phenocrysts are fractured and sliced; the fragments are offset to form a lens shape. The groundmass and albite-oligoclase phenocrysts have undergone extensive sericitization and some silicification.

Secondary cleavage oblique to the primary cleavage is characteristic of ash beds and indicates weak rock. The lavas have one cleavage only and contrast strongly with porphyry, which has cleavage parallel to its outer border and a poor fracture system in its central part. During metamorphism this porphyry behaved as a more competent and brittle rock than the lavas around it.

Vertical Range of the Workings.—Production has been almost entirely from between the surface and 3000 feet depth. Development work has reached 4000 feet depth and the deposits show only slight differences in mineralization at different levels.

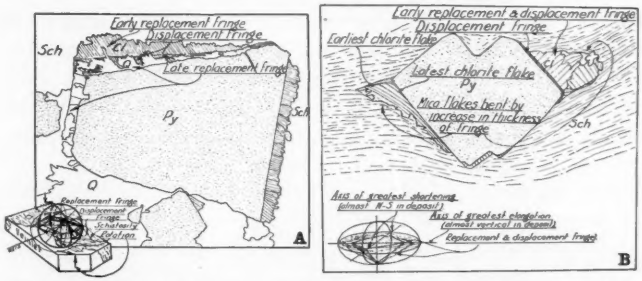


FIG. 4. Typical fringes about metacrysts in wall rock of gold lodes.

a. Rotational Type of Fringe. No. 5 vein, 200 level. Pyrite (*Py*, stippled) is surrounded by two fringes. The outer fringe of chlorite (*Cl*) is a complex type with irregular outer limits. The inner fringe of chlorite has a wedge-shaped cross section and is a displacement type. This inner fringe is almost completely replaced by later quartz which is continuous with quartz veinlets. Chlorite of the inner fringe differs from the outer one in index of refraction and crystal continuity. Complex movements causing rotation of the pyrite and allowing contemporaneous mineralization are illustrated by the inset drawing (lower left).

b. Compressional Type of Fringe. Distant from No. 13 vein, 3625 level. The outer chlorite fringe is well developed along the schistosity and is absent normal thereto. The inner fringe is narrow and has a rectangular cross section. Note that the mica flakes which determine the schistosity are bent away from the fringe at the lower left and the upper right and indicate displacing movements in connection with growth of the fringe. The bent form of the chlorite in the thick part of the fringe at the left shows progressive displacement of the schist outward from the pyrite and along the schistosity. The inset drawing at the lower left illustrates the forces during deposition of this type of fringe.

Mineralization along Lodes.—Wall rock changes occurred partly during regional metamorphism and partly during the subsequent period of mineralization. Chlorite, quartz, and carbonate are common to both phases of alteration, but those of regional distribution are fine textured and possess poor schistose structure whereas those of the mineralization stage are coarser and have an early shear schistosity; massive structure is especially characteristic of the intermediate mineralization stage, and columnar structure of the later stage. Late stage structures are of especial interest because those along medium or rich parts of veins differ from those along average, low grade or barren stretches.

An average mineralized zone consists of a central quartz vein zone, a bordering zone with fine pyrite in carbonated wall rock, and a light colored carbonated zone with sparse, coarse, pyrite extending to variable distance from the zone of quartz veins and metallic mineralization (Fig. 5). Amount of diffusion outward

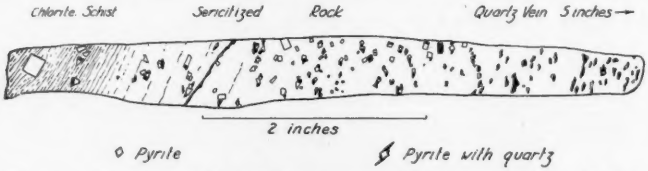


FIG. 5. Camera lucida drawing of part of No. 13 vein, 3250 level, to show typical zones of wall rock mineralization, and mineralization along a low grade quartz vein.

Sericitization and slight carbonatization extend outward from a central quartz vein zone and end abruptly against slightly sericitized and chloritized volcanics. Pyrite increases in size with decreasing abundance and increasing distance from the center of the vein.

from a fissure, now represented by the central quartz stringer zone, seems to have controlled amount and texture of pyritization. Zones of pyrite cubes, with or without associated quartz veinlets, cut the schistosity at a slight angle (Fig. 6-*a*) in the same manner as quartz veins to which they correspond in period of deposition. Pyrite commonly has fringes of quartz, carbonate and chlorite. Some fringes are fillings in mechanical openings; others are meta-

somatic replacements with irregular outer boundaries to the surrounding rock and were made while the rock was subject to stresses similar to those producing the mechanical openings.

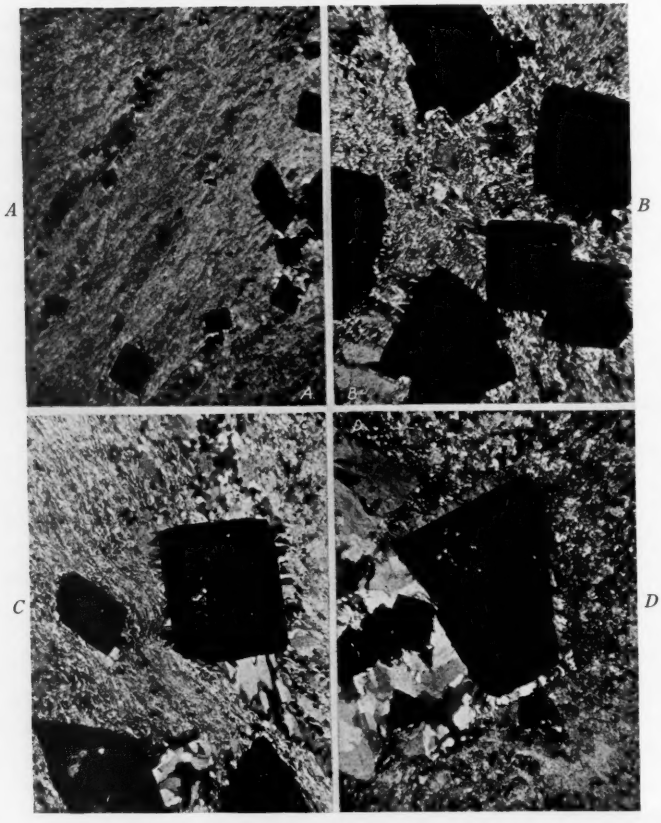
A fissure in pyrite from No. 13 vein on the 3625 level has matched walls with the intervening space filled with columnar chlorite and quartz continuous with the surrounding fringe. The opening of this fissure shows clockwise rotation of the lower part of the central crystal (Fig. 1-*b*). Gold and the associated metallic minerals accompany chlorite in this part of No. 13 vein. Another chlorite fringe from this same locality has the chlorite cleavage parallel to the pyrite face and is replaced and penetrated to variable distances by quartz columns perpendicular to the pyrite (Fig. 3). Accessory mechanical disturbance is shown by minute fault planes in the older chlorite. Generally double fringes with distinct linear outer walls and wedge-shaped cross section are fillings of openings as the space opened up due to mechanical stress rather than replacements influenced by stress in the wall rock. Either mode of emplacement indicates existence of stress which facilitated passage of mineralizing solutions. Method of fixation of a part of the passing solutions is a minor problem within the major one considered in this paper.

Granular carbonated wall rock around many pyrite cubes and their fringes is partly replaced by fringe minerals, so that alteration precedes mineralization and mineralization stresses about pyrite.

Distinction of High and Low Grade Parts of Veins.

Study of high grade sections of veins as distinct from low grade ones, rather than of the Pearl Lake veins as a group, brings out distinctive differences between the two groups. These may be summarized under the following headings, of which the last is most critical.

1. Type of wall rock.
2. Type of pre-mineralization metamorphism.
3. Type of alteration accompanying mineralization.
4. Type of structure produced in wall rock during mineralization.


A
B
C
D

Type of Wall Rock.—Almost any competent rock of the volcanic series, lying within the mineralized belt, is a suitable wall rock; for example, No. 5 vein has spherulitic lava and volcanic tuff, some high grade sections of No. 7 vein and No. 10 vein have tuff with interstratified graywacke bands, and still others have fragmental tuffs or flow tops. Quartz porphyry is unsuitable wall rock and even highly pyritized sections are commonly low grade or barren; but the east end of No. 13 vein has low medium grade ore in porphyry on the 1875 level. Veins cutting through

FIG. 6. Photomicrographs showing variation in wall rock structure with gold content of veins at Pearl Lake.

A. Tuffs along vein 15, 3375 level, showing typical low grade to barren mineralization. Slight mineralization about pyrite (black). X-nicols, × 15.

B. Sericitized porphyry on N. wall of vein 15, 3375 level, showing mineralization along low grade vein. Cleavage extends upward from the bottom at 45° to left, along which the diagonals of the pyrite cubes are oriented, with columnar sericite approximately normal to the faces at their intersection on the cleavage. No introduced mineralization occurs along the diagonal of the pyrite normal to the principal cleavage. Typical of walls of low grade lodes. X-nicols, × 45.

C. Schistose graywacke along 10 vein, 3000 level, showing mineralization typical of medium grade ore. Increased length of columns of quartz (low relief) and carbonate (high relief) in a clockwise direction show clockwise rotational stress about pyrite during mineralization. Irregular outer termination of the columnar minerals indicates some replacement. Asymmetric distortion of the schistosity about the left central pyrite shows clockwise rotation under mechanical stress to give mechanical distortion of the rock. The large pyrite center is surrounded by columnar minerals; other pyrites have columnar minerals on two faces only. Characteristic of medium grade ore; grade is estimated on the basis of percentage showing complete envelopment. X-nicols, × 45.

D. Highly carbonated wall rock along vein 5, 200 level, showing typical high grade mineralization. Pyrite surrounded by outer rim of chlorite (dark) and by inner wedge of quartz (light); increasing width of the wedge in a clockwise direction indicates clockwise rotational stress acting about a point near the left side of pyrite. The outside of the chlorite rim is an indefinite replacement contact but the inner quartz box is sharply limited; matched walls for the quartz are pronounced at right of pyrite. This rotational stress structure is typical of high grade lodes. X-nicols, × 28.

thick series of incompetent ash layers are mostly poor in gold. Much low grade "black sericite schist" along No. 7 vein on the 1875 level is an ash derivative.

The cause of low grade sections is not always evident in the wall rock type as, for example, where No. 13 vein lies in favorable andesite and basalt flows on the 3250 and 3375 levels. Relative physical properties of the two different rock types on opposite sides of the mineralized zone may hold the explanation in some cases. The type of wall rock may serve as a general guide in blocking out areas for exploration but is not an entirely reliable indicator of high or low grade ore; exceptions occur in a sufficient number of instances to indicate that not wall rock, but some other feature associated with certain wall rock types, is probably the real indicator.

Type of Pre-Mineral Metamorphism.—Metamorphism of wall rock preceding metallic mineralization takes two contrasted groups of forms; sericitization, chloritization and epidotization are most common, whereas carbonatization with silicification are less common but more spread out in individual occurrences. Albitization occurs adjacent to porphyry along some low grade parts of veins. Sericitization as a phase of early regional metamorphism or as a very early stage of mineralization alteration, is very general in the volcanics throughout northern Ontario and Quebec. Excessive sericitization of this later period is rare along high grade parts of veins and recurs along low grade stretches.

Epidotization was observed only along high grade parts of No. 5 vein on the 200 level, No. 10 vein on the 3000 level and No. 13 vein on the 2500 and 3000 levels. Chloritization is more general, but is associated more often with high grade than low grade parts of veins. Exceptions occur in the femic tuffs along No. 15 vein on the 3375 and 3875 levels and No. 13 and 14 veins on the 3250 and 3375 levels; carbonatization or silicification, which have been found to be extremely unfavorable, accompany chloritization in these instances.

Carbonatization or silicification or both, of the metamorphic stage, occur along the walls of low grade parts of No. 13, No. 14 and No. 15 veins. No. 3 and No. 7 veins are the only ones

lacking this type of metamorphism. No. 13 vein has extremely mild silicification and carbonatization on the 3000 and 3625 levels and is the only medium or high grade vein showing either change.

Type of Alteration Accompanying Mineralization.—Three types of alteration dominate accompanying mineralization changes in wall rock: sericitization, which is most common, silicification, which is associated with low gold values, and carbonatization, which follows high grade veins. Introduction of chromiferous chlorite, chalcopyrite, tourmaline, albite and adularia represents less common and minor phases of mineralization that have no apparent relationship to distribution of values in veins.

All medium or high grade veins, except No. 13 where it enters porphyry on the 1875 level, show carbonatization of this period. The rich part of No. 7 vein on the 1875 level shows slight sericitization of the late mineralization alteration stage but has carbonatization as the dominant process.

Less than 50 per cent. of the low grade veins exhibit carbonatization; they include No. 13 on the 3125 level, No. 14 on the 1875, 3250 and 3375 levels and No. 15 on the 3375 and 3875 levels, and these have extensive associated silicification. This silicification occurs as a general, irregularly connected mass of granular quartz extending throughout the rock, and should not be confused with the columnar silicification about pyrite metacrysts.

Sericitization is pronounced along low grade parts of No. 3, No. 7 and No. 15 veins and preceded silicification along low grade sections of No. 13 and No. 14 veins. Sericite due to alteration accompanying mineralization is massive except for later cleavage structures oblique to the original schistosity. High grade veins, by contrast, rarely have over 30 per cent. sericitization and the sericite is usually present as parallel flakes or as a lattice of them.

Type of Structure Produced in Wall Rock During Mineralization.—Low grade veins differ from high grade veins in wall rock structures more than in any other characteristic. These significant structures include (1) a cleavage oblique to the principal banding or schistosity and found in thin sericite bands but not pronounced throughout the entire mineralized zone, and (2)

fringes about pyrite and carbonate metacrysts in the mineralized zone.

Oblique cleavage is lacking in the wall rock of high grade veins such as No. 5 vein, and the medium and high grade parts of No. 13 vein on the 1875, 2500 and 3000 foot levels, or is confined to very narrow, completely sericitized bands as in the high grade sections of No. 7 vein on the 1875 level, No. 10 vein on the 3000 level, and No. 13 vein on the 3625 level. These sericite layers average about 1/16 inch thick; cleavage is limited to them and affects a very minor part of the rock. Low grade sections of Nos. 7, 13, 14 and 15 veins have oblique cleavage well developed in wide sericitized layers, or even in the absence of them. No. 3 vein in porphyry on the 1875 level, and No. 15 vein in volcanics on the 3375 and 3875 levels, lack oblique cleavage and are exceptions to the general rule. Minerals and structures of the early period of metamorphism and pyrite crystals are faulted by the oblique cleavage. Extensive silicification, development of massive sericite and introduced mineralization about pyrite are contemporaneous with or later than the oblique cleavage and cross it. Locally tourmaline is faulted by the cleavage and at other places bridges it.

Fringes of quartz, chlorite, carbonate or rarely albite and sericite separate pyrite crystals from the wall rock on two or more faces, edges or corners. One form—the compression type—is associated with all low grade parts of veins and usually with low grade veins only. Another form—the rotation type—is indicative of complex stresses producing rotation to some degree and is associated with high grade veins only. The high grade No. 5 vein has outer fringes of chlorite with indefinite outer limits and sharply defined inner fringes of columnar quartz. Some low grade sections possess neither rotation nor compression structures (Fig. 6-*A*). Carbonate metacrysts along No. 14 vein on the 3250 and 3375 levels have envelopes similar to those about pyrite. Fringes about pyrite metacrysts are no indication of the grade of the adjacent lode; but the type of fringe is a very important indication of the relative gold content.

Minerals Deposited about Metacrysts.—Quartz is the most common columnar mineral in the fringes and in many places is the only one. Fringes along No. 13 vein on the 3625 level have chlorite to almost complete exclusion of other minerals. Chlorite occurs more often than quartz in fringes along high grade veins. Quartz and albite, frequently continuous with small veins bordering the main one, surround pyrite along No. 15 vein on the 3375 level; quartz fringes about pyrite along No. 5 vein are continuous with quartz veinlets (Fig. 4-*a*).

Pyrite crystals have fringes of gold in some rich pyritic schists. Small minute boxes of gold about pyrite have linear inside and linear or irregular outside borders similar in every respect to those of the gangue minerals. More often the boxes are a composite of gold and gangue, as in No. 13 vein on the 3625 level. Commonly sericite is recrystallized perpendicular to the face of the pyrite most nearly normal to the principal schistosity; this structure is especially well developed in the low grade tuff part of No. 7 vein on the 1875 level, No. 14 vein on the 3250 and 3375 levels and No. 15 vein on the 3375 level.

Interpretation of Results.

Details of fringes that are of diagnostic importance are so elusive that specimens for comparison are often necessary to study any new series. However, practical tests of this method of distinguishing high grade lodes from low grade ones have demonstrated the practicability of this method and show that it may be relied upon to give a correct estimate in eight cases out of ten. Therefore the following is not intended to elucidate the distinguishing features of the fringes but is an attempt to explain why peculiarities of the fringes should measure degree of gold mineralization of a lode in a district known to contain gold lodes.

Mineralization on all faces of pyrite, as found along high grade parts of veins, was due to rotational or irregular complex stresses in the rock, opening it in all directions to mineralization processes and gold deposition. It is in just such openings that minerals are deposited or along such stress lines or potential openings that replacement occurs and where much wall rock gold is found.

Wall rock stresses increase mineralization about pyrite and an equal increase is to be anticipated in the adjacent veins; fillings and replacements along secondary openings made by these stresses carry most of the gold and gold-bearing minerals of the lodes.

Secondary oblique cleavage and asymmetric crumpling in highly sericitized rocks indicate that such rock is subject to facile readjustment to stresses before mineralization can occur and therefore is unfavorable to mineralizer penetration. Bulging cleavage planes in rock about pyrite metacrysts show that these are competent to take lateral stress for a time; it is during existence of this differential pressure that the minerals are deposited along the plane of least pressure in the rock (Fig. 4-*b*). Stress is gradually taken up by the molding of the wall rock to the shape of the vein or piece of pyrite, instead of being transmitted as a fracturing force.

Rock lacking oblique cleavage is more competent to transmit stress. Oblique stress in competent rock causes rotational stress about pyrite and progressive change of location of point of maximum and minimum pressure, so that the metacrysts may become almost completely enveloped in late-stage minerals. Stress oblique to the quartz veins in competent rock is transmitted to them and causes fracturing and makes channelways for mineralizing solutions.

Description of two veins in the McIntyre mine, Nos. 5 and 13, will serve to illustrate the correlational value of the criteria and the significance of most of the features observed in the deposit.

Description of the Veins.

The high grade No. 5 vein on the 200 level lies approximately along the contact of dark colored volcanic tuff and a perlitic, vesicular flow-top. Zoisite and quartz areas in the tuff preserve outlines and remnants of plagioclase laths. Alteration chlorite occurs along the poor cleavage but sericite is almost absent. The rocks are highly and irregularly changed to coarse carbonates that cut the schistosity; these belong to the later mineralization stage rather than to early metamorphism. Pyrite metacrysts are abundant in the mineralized zone and are surrounded on all sides

by columnar minerals or are cut by irregular veins of them. Many record two periods of major stress by separation of an early outer envelope of quartz and chlorite from the pyrite by a later inner one of columnar quartz or chlorite (Fig. 6-*D*).

No. 13 vein is well developed through great vertical range, and ore grade fluctuates from low to medium; it is one of the few veins that carry medium ore in porphyry. Dark green porphyry wall rock at the east end on the 1875 level is slightly schistose and has chlorite and sericite along shear cleavage about quartz phenocrysts. Remnants of porphyry groundmass show extremely fine texture. Less than 10 per cent. of the extremely fine pyrite crystals have rotational fringes; this is an extremely low percentage for medium ore.

Dark gray, spherulitic dacite forms wall rock along a high grade part of No. 13 vein on the 2500 level. Chloritized streaks, zoisitized oligoclase and rare sericite on prominent shear planes represent regional metamorphic changes. Late carbonatization is superimposed on other changes in the intermediate part of the mineralized zone. Strong rotational stress structures border fine pyrite, especially close to the vein zone, but are not pronounced in areas of excessive sulphide mineralization or far from the vein.

A dark colored, fragmental flow-top or tuff forms walls for No. 13 vein on the 3000 level. The matrix was extensively chloritized and slightly sericitized and even carbonated during the metamorphic stage. Later sericitized shear zones cut pyrite, and abundant coarse carbonate of the mineralization stage obliterates many of the early structures. Pyrite crystals in the slightly mineralized rock distant from the vein show no rotation but those in the chloritized and carbonated walls are surrounded completely by fringes of columnar quartz and chlorite and massive carbonate. Pyrite is variable in size.

A low medium part of No. 13 vein on the 3625 level is in fine, dark green rock with light, yellowish green sericite bands of volcanic ash between coarser tuff layers. The rock was slightly silicified during the metamorphic stage. Pyrite distant from the vein is up to ½ inch across and in some cases shows mild rotation. Chalcopyrite veins cut pyrite. The rock becomes finer textured

adjacent to the vein and is composed of up to 25 per cent. sericite bands with oblique secondary cleavage. The wall rock is heavily carbonated and cut by later veins with albite, quartz and carbonate, or more often is replaced by adularia and tourmaline needles.

Commonly the quartz of No. 13 vein disappears on the 3625 level and the mineralized zone continues as high grade pyritic schist in dark green fragmental rock containing very little sericite, much introduced chlorite and a great abundance of pyrite about 1/12 inch across. About one per cent chalcopyrite occurs as dustlike areas through the rock. More than 50 per cent of the pyrite shows structures indicative of rotational stress (Fig. 1-*b*). Local shear planes cut off occasional metacryst bulges about pyrite to produce "nonconformity" in the cleavage. Chlorite occurs in envelopes about the pyrite to almost complete exclusion of quartz.

No. 13 vein has low grade stretches as well as the high grade ones described already; these occur between both porphyry and volcanic walls. The vein enters dark silicified and sericitized porphyry at its east end on the 3125 level. The rock is 50 per cent sericitized, and change is almost complete along weak schistose zones with secondary oblique cleavage. Heavily mineralized wall rock contains up to 10 per cent schistose carbonate with structure parallel to the early cleavage, showing that the carbonate belongs partly to the early metamorphic stage. Alteration stage carbonate cuts across the rock cleavage and replaces all other nonmetallic minerals. Fine pyrite has numerous compression structures but has none of the rotational type. Associated quartz veins are slightly granulated and replaced along granulated zones by carbonate and chalcopyrite.

Lit-par-lit injections of porphyry extend along No. 13 vein for 75 feet west from the main body on the 3125 level but light gray tuffs are the chief wall rock. Vesicles have been slightly deformed and the rock chloritized locally; blue quartz veins cut it at frequent intervals. Parallel alignment of sericite in certain bands gives the rock a poor schistosity. Tendency to an oblique cleavage is indicated by asymmetric crumpling in the more schistose bands. Abundant fine pyrite crystals lack rotational fringes

but have compressional type chlorite fringes at the ends of pyrite. No carbonatization was observed.

Dark green, nearly massive andesite or basalt, with obscure flow banding and much chlorite, forms walls of No. 13 vein in a low grade section on the 3250 and 3375 levels. The light yellowish, mineralized zone has a sharp, distinct outer boundary; pyrite cubes attain 1/4 inch across a face in unaltered walls whereas in the mineralized band they do not exceed 1/8 inch and decrease to 1/20 inch with increasing mineralization near the vein (Fig. 5). Quartz and pyrite veinlets occur in the mineralized zone at intervals. Undeformed tourmaline and leucoxene lie along irregular, oblique secondary cleavage and in mineralized zones and indicate that these minerals are relatively late ones. Compressional fringes of quartz are the only types observed about pyrite in the mineralized zone. Sericite is the chief alteration mineral but irregular silicification outwards from a stockwork of fractures is prominent on the 3375 level; sericitized cores indicate that sericitization preceded silicification and the accompanying carbonatization. Pyrite in the silicified zone is in minute cubes (1/40 inch) or as an aggregate of fine grains.

WALL-ROCK MINERALIZATION AT KIRKLAND LAKE, ONTARIO.

Introduction.

Kirkland Lake, the second great gold-producing area to be opened in Canada, lies sixty miles southeast of the Porcupine district and five miles east of Swastika on the Nipissing Central Railway. Gold occurs in quartz veins and as a replacement of chloritized and carbonated wall rock along a fault zone; it is mainly in metallic form and is recovered by cyanidation, although some in the tellurides sylvanite, calaverite, and petzite is partly lost by this process. During 1931 the camp produced 1,700,895 tons of ore valued at $12.81 per ton. Ore below $10 would be considered low grade whereas $20 is high grade. Costs average about $6.50 per ton so that rock below $6 grade is non-productive.

General Surroundings of Veins.—The mineralized fault zone and subsidiary fractures are in intrusive augite syenite and a

variety of porphyries. Augite-rich syenite or "lamprophyre" is considered unfavorable wall rock, but both albite porphyry and orthoclase porphyry likewise have low grade sections. Augite of the lamprophyre type commonly shows augen form adjacent to the fault plane and is changed to a sericite-quartz-albite-epidote mixture up to forty feet away from the ore zone. Orthoclase is replaced extensively along numerous fractures by carbonate and chlorite. Augite content decreases eastward, and the crystals are less distorted and angular fractures are more common in that direction in the fault zone. Characteristic alteration of augite continues, but chlorite becomes as abundant as carbonate in veins and feldspar replacements; sericite is common.

Vertical Range of Workings.—Three mines have shafts below 4000 feet. Most of the specimens collected for study were taken from the 19th (2375) and 20th (2500) levels of the Teck Hughes mine. These specimens come from a limited section but show no major difference in mineralization from some obtained from higher levels in 1928, or others from even closer to the surface which the author had an opportunity to study in 1925.

Mineralization along Lode.—The deposit lacks the diversity of wall rock of the Pearl Lake lodes and is more regular in major mineralization features and has more subtle differences of mineralization along high and low grade parts. Major simplicity may be attributed to the fact that changes belong to overlapping stages of a single period and are centralized along the fault fractures. Todd [7] describes the augite syenite as

> becoming reddish and developing a less femic aspect adjacent to fractures or later intrusives or where gases and solutions have circulated. Augite changes to a light green, carbonate, sericite, feldspar, epidote mixture, and orthoclase is sericitized slightly and replaced along fractures by chlorite and carbonate which also fill the fractures.

Perthite replacements of dusty orthoclase walls border many fractures in augite syenite, especially the large early ones with quartz, and appear for some inches outwards as white feldspar grains and discrete crystals in red syenite. Quartz filling, perthite al-

[7] Todd, E. W.: *Op. cit.*, p. 27.

teration and production of the red syenite bordering the fault zone, represent the initial stages of mineralization.

Both quartz and wall rock are mineralized by late carbonate, chlorite and sericite; only altered augite resists extensive replacement. Mineralization follows fracture planes and even the most mineralized sections preserve a fracture pattern in the angular form of unreplaced rock and linear distribution of rock residuals (Fig. 2). Initial stages of mineralization are represented in least changed sections; fracture walls match and are commonly filled by columnar chlorite or carbonate, or rarely by schistose minerals where mineralization is low. Areas of more intense mineralization have unmatched walls penetrated by columnar chlorite and carbonate aligned along an angular vein net-work laid out by original fissures. Replacement has widened fissures through feldspar to veinlets one or more millimeters across. Increased mineralization is indicated by irregular areas of matted and bladed chlorite and granular carbonate in the residual rock between veins of the angular network; replacement of this degree commonly averages over 30 per cent. change, and the original rock is almost completely destroyed locally. Fig. 2-*B* illustrates replacement for a general area and Fig. 7-*D* shows great local intensity in a part of this area.

Metallic mineralization in the quartz veins and wall rock favors areas where the above mineralization is most pronounced and the gold content of the mineralized zone is approximately proportional to the degree of widening of the veinlets by wall rock replacement. However, the requisite degree of replacement for a specific gold content varies for each rock type.

Distinction of High and Low Grade Parts of the Deposit.

Todd[8] noted that the "lamprophyre" phase of the augite syenite was unfavorable to values, and emphasized type of wall rock. However, contrast of mineralization along high grade stretches with that along low grade parts points to degree of alteration replacement as the most important index of values;

[8] Todd, E. W.: *Op. cit.*, p. 92.

nevertheless composition of wall rock and structures associated with values greatly modify the general interpretation of requisite degree of replacement alteration. These factors may conveniently be considered under the headings:

1. Effect of structures accommodating mineralization.
2. Effect of wall rock undergoing mineralization.
3. Types of replacement alteration minerals.
4. Unrelated mineralization.

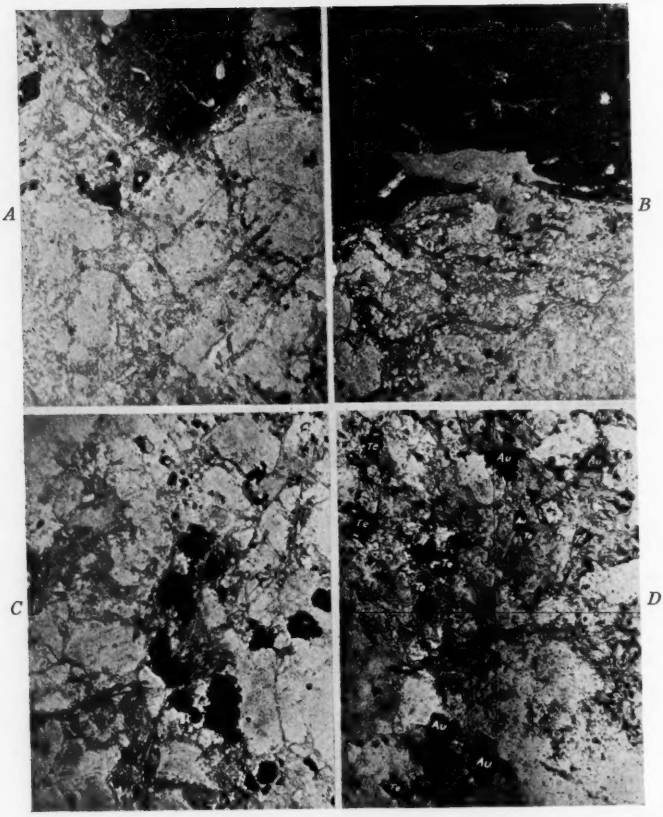
Effect of Structures Accommodating Mineralization.—Mineralization is essentially the same in the Main ore zone and in branching fractures; it follows openings produced by the fault movements. Movement produced either parallel shear planes or intimately crushed rock along one shear or between two shears. Shears are subparallel and rarely opened the ore zone to intimate penetration by replacing solutions. Schistose chlorite or sericite fills openings in orthoclase porphyry west of the Central shaft, in dark albitic aplite in the same part of the mine or in aplitic albite porphyry between the shaft and the Lake Shore boundary on the 19th level. Alteration replacement is very limited and metallic mineralization poor where openings were narrow and limited in distribution. Shear movements opened dark albitic aplite on the 20th level near the western diabase dike to allow extensive replacement, but even here they are helped by complex crush openings with columnar minerals.

Crush openings form an extremely irregular, extensive network where fragmentation increased at each renewed movement. They are the most common type along the Main ore zone and subsidiary branches, and were studied in syenite, albite porphyry and quartz veins but probably affect all rocks. Augite-rich syenite usually shears instead of cracking; on the other hand albite porphyry breaks at a few points only. Syenite of intermedite composition, such as that on the 19th level along No. 3 vein and also north of the Main ore zone at the Lake Shore boundary has undergone greatest degree of shattering during the replacement alteration stage which is associated with ore deposition. Mixed rock types and discontinuity of quartz veins in the ore zone cause

heterogeneity and shattering almost as great as in the syenite, as for example in the Main ore zone between the 19th and 20th levels in the east part of the Teck Hughes.

Intimate cracking during the mineralization stage and extensive mineralization of the fissures does not necessarily indicate a high grade lode but for the most part is close to an ore shoot, and shattering may extend beyond one. For example, the grade is low in shattered rock along No. 3 vein south of the Central shaft on the 19th level, and the nearest high grade ore is 40 feet above. Similar low grade rock adjacent to the Kirkland Lake boundary is intimately crushed and lies along the prolongation of a shoot worked in the Kirkland Lake mine (Fig. 7-*B*).

Effect of Wall Rock Undergoing Mineralization.—Metallic mineralization is associated with replacement alteration. Augite syenite bordering high grade deposits along No. 3 vein and the Main ore zone adjacent to the Lake Shore boundary is 30 to 35 per cent. altered and replaced; it is only 10 to 15 per cent. replaced along the low grade part of No. 3 vein on the 19th level. Syenite is 25 per cent. altered and replaced along the low grade part of the lode on the 20th level adjacent to the Kirkland Lake mine; however, the replacing minerals are principally those left by highly penetrating solutions such as deposited the carbonates early in the replacement series and antedate metallic mineralization. Observations in the syenite indicate high values where replacement, especially by chlorite, exceeds 30 per cent. and low values where it falls below 15 per cent. The amount varies greatly with the type of rock. Quartz, for example, is less than 20 per cent. replaced in the very high grade part of the ore zone between the 19th and 20th levels, and low average ore occurs in albite porphyry on the 19th level and other parts of the mine where the wall rock is only 10 per cent. replaced. High replacement alteration, as an indicator of ore values, requires qualification of "high" in terms of type of wall rock. Although 25 per cent. replacement is considered low in augite syenite, 10 per cent. is high in quartz and albite porphyry. Subject to this restricted use, high replacement alteration of the mineralization stage accompanies high values and low replacement alteration, low values.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Type of Replacement Alteration Minerals.—Minerals of the replacement alteration stage are a definite group in which chlorite occupies a leading place; they follow shear zones and crush fractures and are confined mainly to the mechanically produced openings in low grade parts of the deposit but also fill large replacement expansions along high grade shoots. Sericite, carbonate and chlorite occupy these enlargements; chlorite veins cut the other two and indicate that chlorite is the later. Metallic mineralization is more specifically associated with chloritized areas than with carbonated or sericitized ones.

Carbonate is more abundant in narrow fissures and chlorite is confined mostly to the wider ones where the two minerals are approximately equally abundant. Extensive carbonate replacement occurs along low grade parts of veins where carbonate dominates over chlorite, as in the low average part of No. 3 vein

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FIG. 7. Photomicrographs showing variation in wall rock mineralization with grade of ore at Kirkland Lake.

A. Augite syenite showing mineralization typical of very low grade part of Main ore zone. Augite (dark) at top is highly altered. Orthoclase (white) is cut by carbonate veinlets (gray) with irregular replacement borders. Degree of replacement and metallic mineralization is low and chloritization almost lacking. Contrast this with high replacement alteration by chlorite along a high grade vein in similar rock (Fig. 7-*C* or 7-*D*). × 24.

B. Augite syenite in contact with west diabase, showing mineralization typical of non-productive part of Main ore zone. The diabase (very dark) is cut by unmineralized chlorite (*Ch*) and is bordered locally by mineralized, uralitized chlorite (*Ch. U.*). Slightly uralitized chlorite veins and carbonate veins (gray, high relief) cut the brecciated feldspar (white). Metallic mineralization is sparse and in the dark early chlorite areas. × 24.

C. Augite syenite along vein 3, showing association of medium rich metallic mineralization with extensive chloritization. Gold, pyrite, and tellurides (black) occur in chlorite (dark) replacing orthoclase (white). Metallic mineralization in unchloritized areas is negligible. × 24.

D. "Green" syenite from upper levels, showing increase of metallic mineralization with increased chloritization. Chlorite (*Ch*) replaces orthoclase (white). Gold (*Au*) and tellurides (*Te*) occur in the chloritized zones and are lacking in the orthoclase. This represents an extremely high grade part of the deposit. × 24.

on the 19th level and the low grade part of the Main ore zone adjacent to the Kirkland Lake mine on the 20th level. Abundance of chlorite in this deposit therefore measures to some degree the freedom of passage of solutions during metallic mineralization.

Unrelated Mineralization.—Three phases of mineralization were observed to be unrelated to ore values: they are early perthitic injection along both high and low grade sections, change of chlorite to uralite adjacent to the diabase dike on the Kirkland Lake mine boundary, and the late quartz-carbonate-chlorite veins that cut the metallic minerals, the ore zone and the diabase dike. The perthite change is responsible for the light color adjacent to solution channels antedating the principal quartz veins; association with all grades of ore relegates it to an insignificant position so far as search for ore shoots in a known deposit is concerned. Minute spearlike crystals of uralite after chlorite are undeformed except on major shears and are undamaged by movements opening fissures for metallic mineralization; they replace carbonates and penetrate sulphides and tellurides. Penetration of metallic minerals by uralite indicates replacement of the metallics and places metallic mineralization antecedent to recrystallization associated with the diabase. The last set of chlorite, carbonate, quartz veins cut the metallic mineralization, the uralitized chlorite, and the diabase. All metallics in them are included mechanically.

Interpretation of Results.

Details of degree of replacement are extremely complex; they involve type of rock subjected to solution attack, content of chlorite relative to carbonate in the group of replacement minerals, and the structure of the replacement products. The importance of the latter is brought out by the fact that it is possible both to select specimens from high grade sections that show erratic and deficient replacement alteration and also to choose promising specimens from low grade sections. However, practical tests using degree of replacement alteration as a measure of gold content of the lode for a reasonable distance on either side of a specimen gave a correct estimate in more than 75 per cent. of the

specimens used; the remaining specimens had a very erratic intensity of replacement; where this erratic behavior is noted, the error is reduced greatly by use of check specimens. Therefore this method of identification of grade is applicable and the following is not a further elucidation of details of replacement but is an attempt to explain why intensity of replacement should measure the gold content of the adjacent lode in brittle rock.

Gold and metallic minerals associated with gold accompany the chlorite of the replacement alteration stage and were deposited by solutions that entered all parts of the rock penetrated by solutions which deposited chlorite. Therefore, degree of opening of the rock to chlorite mineralization measures its degree of opening to gold mineralization. Slip or schistose chlorite in veins is less favorable than columnar chlorite because it indicates a combined shearing and compressional stress which was narrowing the width of the opening between the walls as the minerals were deposited to fill the space between them.

Replacement of the walls indicates a greater excess of solutions and hence greater amount passing than is indicated by simple fissure filling. These replacements represent only a small side current from the main body of the solutions and hence a much more intense mineralization than fissure filling. Chlorite in them is matted and not columnar as in the fissures. Amount of chlorite of this stage indicates amount of possible mineralization but not amount of gold. If a district has gold mineralization, then the amount of chlorite replacement of this stage measures its gold mineralization possibilities; if a district has no gold mineralization, then the chlorite mineralization can be of no critical value.

Solutions that deposited carbonate began to be introduced slightly in advance of those that left chlorite, and overlap it in period of deposition. Also carbonates appear in narrower veins and solutions depositing them appear to have been able to penetrate smaller openings than those which brought in chlorite. Many openings open to carbonate mineralization, were not open to chlorite and gold mineralization and hence carbonate is not as critical a mineral as chlorite.

Most of these details of mineralization and associated wall rock alteration features are illustrated by the following examples.

Descriptions of Veins.

The Main ore zone and No. 3 vein are both worked at the 19th level of the Teck Hughes mine. The Main ore zone, and principal producer, is just south of the Central shaft and is high grade most of the distance to the diabase dike at the Lake Shore boundary. No. 3 vein is forty feet farther south at the level but is only ten to fifteen feet away about forty feet above; it is moderately high grade west of No. 16 crosscut.

Mineralization along No. 3 Vein.—A low grade part of No. 3 vein south of the Central shaft on the 19th level is in augite syenite composed of about 30 per cent. augite, 5 per cent biotite, and 1 per cent. each of magnetite and apatite. Syenite in No. 16 crosscut is less femic than in the stope and farther west and has up to 5 per cent. of slightly sericitized groundmass between orthoclase with perthitic borders. The syenite begins to be spotted with red at about ten feet from the vein and is speckled with white perthite for about one inch away from it. Augite has disintegrated without change of form to a light green aggregate of quartz and carbonate with subsidiary sericite and magnetite. Biotite over one inch from veins is under 10 per cent. leucoxenized.

Later changes are superimposed on this slightly altered wall rock and the early quartz veins. For example, mineral boundaries, are displaced along shear zones having chlorite approximately parallel to the plane of shear with columnar chlorite drawn out *en echelon* by later movement. This introduced chlorite is slightly earlier or contemporaneous with irregular, columnar or aggregate chlorite in filled and replacement veins in othoclase; these fray out in augite almost as they enter it or become very indefinite irregular impregnations. Irregular replacement is less frequent in feldspar and is accompanied by disseminated carbonates approximately equal in abundance to chlorite. Chlorite is limited generally to wider veins, whereas carbonate occupies the extremely minute ones and indefinite discontinuous openings.

Highly chloritized feldspars, sericitized groundmass, and to a lesser extent altered augite, have extensive pyrite mineralization. Aggregate sericite is associated with pyrite but chlorite forms a "wrapper" that separates pyrite from sericite, and radiating bunches of chlorite are usually abundant in the vicinity.

By contrast, the vein is high grade only thirty feet to forty feet above the 19th level. Augite syenite with higher content of microporphyritic groundmass of small albite laths in an even finer matrix, forms the walls. Stages of alteration are similar to those found along the low grade section and differences are in intensity rather than in type. All biotite is leucoxenized and orthoclase is 25 per cent. changed to perthite. Alteration and replacement outward from cracks is 30 per cent complete and has spread from cleavages and Carlsbad twin planes in places; only angularity of the replacement patterns indicates any original fissure planes (Fig. 7-*C*). Even augite is veined. Carbonate predominates locally but chlorite is approximately equal in importance. Chlorite replacement of carbonate along cleavage planes suggests that chlorite mineralization may have continued after carbonatization ceased. Chlorite replacement follows veins in a majority of cases whereas carbonate is more general.

Mineralization along Main Ore Zone.—The Main ore zone traverses a greater range of rock types, exhibits a greater range of intensity of alteration and has greater variation in gold content than is found in No. 3 vein. It is very high grade at the 19th level adjacent to the Lake Shore boundary. Augite syenite with albite-rich aplite interstitial to the orthoclase forms the north wall. Apatite is abundant and abundantly fractured. The walls are cut by complex carbonate veins containing albite and are in places traversed by albite stringers. Perthite replacement is common adjacent to the smaller veinlets. Augite is altered to carbonate and chlorite and partly replaced by the latter. Orthoclase is 20 to 70 per cent. replaced, averaging about 35 per cent.; by carbonate and chlorite; columnar and aggregate types are common and slip and schistose forms are rare. The minerals are in part contemporaneous but chlorite seems to have continued to a

later period and the carbonate to have invaded smaller fissures during early replacement alteration.

Metallic mineralization is in areas of greatest chloritization in orthoclase and is rare in augite or slightly changed feldspar. Maximum chloritization rather than average change seems to be the important factor.

The center of the zone resembles a gouge and consists of many sliced orthoclase fragments and interspersed quartz veins. Intense changes just preceding and accompanying metallic mineralization obliterate early metamorphic changes. A network of columnar chlorite veins cuts quartz veins and orthoclase fragments; in feldspar they have irregular replacement walls and great irregular bordering masses of aggregate chlorite; feldspars are over 50 per cent. chloritized and about 10 per cent. carbonated. Replacement in quartz does not exceed 10 per cent. Metallic mineralization is confined to these chlorite-carbonate filled fissures or to replacement enlargements along them. Drag and imbricate structure of columnar carbonate and chlorite indicate later deformation, and along some veins metallic minerals have been ground to black powder and the chlorite changed to sericite.

The very rich siliceous section of the ore zone in the eastern part of the Teck Hughes continues down to the 20th level at 125 feet below; this rock type is not usually susceptible to extensive replacement but here it is 20 per cent. changed over a wide zone. Chloritization is general, and is weak only over very small areas almost completely lacking metallic mineralization. Columnar chlorite in veins transverse to the ore zone is frequently rotated parallel to the plane of shear and the metallic minerals ground to powder.

By contrast, the ore zone is low grade at this level at the west side of the Teck Hughes. A shoot of ore grade rises eastward in the Kirkland Lake mine towards the Teck Hughes ground between the 19th and 20th levels but is not worked in the latter mine even although a drift followed the vein westward to the diabase dike on the boundary. An extremely complex group of feldspar porphyry, dark aplite and augite syenite forms wall rock and the gold averages below productive grade. At a distance of less than

100 feet from the shoot, alteration is very slight. Augite is altered to a complex fine aggregate of chlorite and epidote, and orthoclase adjacent to the quartz stringers is injected with perthite but the rock is only 10 to 15 per cent. chloritized and 3 per cent. carbonated; about 50 per cent. of these secondary minerals are in filled fissures and the remainder are replacements along them (Fig. 7-*A*). Metallic mineralization favors areas of greatest chloritization but commonly is in small chlorite veins converging on replacement enlargements.

Chlorite adjacent to the diabase dike has been converted to acicular uralite and both diabase and veins are cut by later barren, unmineralized chlorite. Metamorphism of the minerals of the ore zone by the heat of the intrusive signifies that the metallic mineralization was complete before intrusion of the diabase. Gold values in the diabase are introduced mechanically during later faulting.

Importance of the relationship of extensive replacement of wall rock, and even of quartz, to the high grade parts of lodes is amply emphasized by some exceptional specimens from the higher levels. Augite syenite with interstitial aplite contains about 2 per cent. of gold and a lesser amount of telluride and pyrite mineralization at one place (Fig. 7-*D*). Augite is changed to a dusty chlorite-magnetite aggregate which is very distinct from chloritized feldspar. Chlorite and carbonate occur along zones of a fracture pattern (Fig. 2); chlorite is so dominant that the syenite is green. Columnar and aggregate minerals are most common and schistose types are almost lacking. Amount of chlorite replacement alteration is practically proportional to gold values. However, this general rule is sometimes affected by carbonate alteration associations and types of walls to the fractures. Carbonate is almost as significant as chlorite where it has 20 to 30 per cent. of associated chlorite.

Poor mineralization and low average values are associated with very slight replacement by quartz-sericite-carbonate veinlets in albite porphyry above the 19th level. Locally, sericite replaces 50 per cent. of the groundmass and the replaced section is min-

eralized with pyrite and tellurides. The rock as a whole, however, does not show more than 10 per cent. change and syenite showing even much greater alteration is confined to barren or non-productive sections.

In general, albite porphyry or quartz walls are less affected by chloritization and carbonatization than syenite. Quartz lodes cut by later chlorite-carbonate veinlets rarely show more than 20 per cent. replacement even in areas with 2 per cent. of gold and tellurides. The general fracture form of these replacements is conspicuous; nevertheless high grade parts are associated with fractures enlarged by replacement even although amount of replacement is low in comparison to that in augite syenite.

WALL-ROCK MINERALIZATION AT RED LAKE, ONTARIO.

Red Lake, the third ranking gold camp in Ontario, is situated in the northwestern part at about 87 miles northwest from Sioux Lookout on the Canadian National Railway. Materials must be taken in by aeroplane or by water in summer or by sleighs in winter. The gold is in coarse metallic form in quartz veins in an albite porphyry "dike" and included schist; it is recovered by cyanidation after crushing to 40-mesh. No special attempt is made to recover the small amount in tellurides. The camp produced $613,471 in gold during the first nine months of 1931. Ore averages about $4 per ton, and costs run between $3 and $3.50 per ton.

General Surroundings of Veins.

The veins do not extend beyond the albite porphyry and are much higher grade in the north part of it than in the southern half. The dike is nearly vertical and, at the Howey mine, cuts schistose volcanics dipping 70° to 80° northward at about 20° northeasterly from their strike; further west the dike intrudes granodiorite, which occurs also north of the mine. The dike is greatly expanded along certain bands in the volcanics and contracted at others; it is sheared and broken at constricted sections and along schist inclusions and has veins along the break zones.

Mineralization along Lode.

Wall-rock mineralization at Red Lake is almost negligible but does occur along some of the higher grade veins; most veins would be considered low grade or non-productive in either the Pearl Lake or Kirkland Lake camps if values over stoping widths are considered as the grade of the deposit. High grade lodes at Red Lake should be compared with medium or even low grade ones at Kirkland Lake and Pearl Lake. Phenomenally high values occur in narrow quartz veins and wall rock is mostly barren.

Two distinct types of mineralized zones occur in the Red Lake deposit: one type resembles brecciated zones at Kirkland Lake in structure and wall rock mineralization; the other type is similar in structure and wall rock mineralization to the Pearl Lake deposits. Each type has 25 to 50 per cent. lower wall rock mineralization for the grade of ore than is encountered at Pearl Lake or Kirkland Lake. The Pearl Lake type of vein is most frequent at the east end of the dike whereas the Kirkland Lake type is most common at the west end.

Mineralized Zones.

Deposits are classed into their respective types and contrasted with the Pearl Lake and Kirkland Lake deposits to bring out application of some of the principles developed there, rather than grouped into high and low grade classes to help geological study at Red Lake. This camp serves as a representative example of use of data collected in one part of the Canadian Shield to development of a new deposit in a similar region.

Pearl Lake Type of Mineralized Zone.—High grade quartz stringers cut heavily mineralized sericite schist in albite porphyry just west of the McIntyre-Howey boundary. The schist has much irregular or augen-shaped pyrite with the greatest length along the schistosity, and carries low gold values. Biotite occurs adjacent to the pyrite along the continuation of the long axis but the flakes possess no fixed arrangement. Muscovite flakes cut and replace the biotite and even pyrite locally. Occasional kaolin

is present close to the veinlets. Distribution of biotite along the long diagonal of pyrite cross-sections is similar to that in compressional stress structures along low grade veins at Pearl Lake where this deposit would not be considered up to average grade.

Albite porphyry on the boundary line is highly sheared and changed to sericite schist with a central lenticular quartz vein up to 16 inches thick. The quartz carries up to $20 of gold per ton. Sericite schist walls have occasional small pyrite crystals with the long diagonal lying along the schistosity, but carry no gold; corners of pyrite along the short diagonal are frequently sheared away. Columnar quartz and rare biotite are deposited as "compressional structures" on pyrite and less often on carbonate metacrysts.

Kirkland Lake Type of Mineralized Zone.—Movement on fracture planes along the Kirkland Lake type of deposit is not great and mineralized zones are extremely discontinuous even where they show most features common to their type. One fracture system begins at the south side of the porphyry near the Howey-McIntyre line and strikes diagonally across the dike to pass out on the north side at about 250 feet west. The best part of this zone carries about $20 per ton over 8 feet of irregular quartz stringers containing fractured pyrite with galena, sphalerite, chalcopyrite, gold and krennerite. Occasional metallic minerals extend into the walls, and the adjacent rock is approximately 15 per cent. changed to dark olive green chlorite. The porphyry is highly sericitized throughout and carbonated locally. Carbonatization and chloritization do not extend more than an inch from the walls of quartz veins and are limited to high grade parts.

Another similar narrow fracture system, about 30 feet to the northeast, has quartz veins up to a foot wide with very high gold values. The wall rock is about 5 per cent. carbonated and carries about 1 per cent. of dark olive green chlorite, some pyrite and occasional tourmaline. Columnar quartz is common around pyrite in the wall rock. Mineralization resembles in type and amount that encountered along the low medium part of the ore zone at Kirkland Lake, and ore average over stoping width falls in that class.

SUMMARY OF RELATION OF WALL ROCK MINERALIZATION TO ORE VALUES.

Consistent association of one set of definite mineralization features with wall rock along high grade lodes, and consistent association of another definite set of features with wall rock along low grade gold lodes, has been determined by study of specimens from deposits of known grade, checked by use of unknown test pieces and applied to evaluation of newly discovered camps, and seems to indicate that the following observations should be of use to geologists studying gold deposits of the Pearl Lake or Kirkland Lake type.

1. Wall rock mineralization along gold lodes affords a rough measure of the ore value in a sufficient number of instances to make it an important aid to interpretation of diamond drill results.

2. Rotational type fringes on pyrite indicate high grade lodes in the Pearl Lake type of deposit. Compressional type fringes indicate low grade lodes. Absence of fringes about pyrite metacrysts indicates barren or non-productive lodes.

3. Relative amount of replacement of feldspars and the groundmass of brittle intrusive rocks by chlorite affords a measure of the grade of ore in the adjacent lode in the Kirkland Lake type of deposit.

4. These criteria are unreliable where vein quartz makes up a large part of the specimen being studied; they apply only to wall rock adjacent to the lode.

AMHERST COLLEGE,
AMHERST, MASS.

THE TEMPERATURE OF FORMATION OF THE MISSISSIPPI VALLEY LEAD–ZINC DEPOSITS.

W. H. NEWHOUSE.

NEW information has been obtained which makes it possible to give definite figures on the temperature of formation of deposits containing sphalerite.

The Mississippi Valley lead-zinc deposits have been chosen for first study.

Liquid inclusions containing a bubble are present in sphalerite. These inclusions are commonly found of large enough size so that temperature determination may be made by heating the mineral on the stage of a petrographic microscope.

DETERMINATION OF TEMPERATURE OF CRYSTALLIZATION OF SPHALERITE.

The liquid inclusions in single crystals of sphalerite constitute an almost ideal means for the determination of its temperature of crystallization. The temperature determination is free from the usual theoretical and practical difficulties which have beset most former workers on fluid inclusions, unmixing of solid solutions, and paramorphic forms.

Two chief difficulties have been present in most of the work thus far done on liquid inclusions as a means of determining the crystallizing temperature of the host. The first is that the inclusions are mostly small, and are commonly composed of more than two phases. It has been necessary in general to use calculations involving extrapolation of known curves in order to obtain the desired information. The second difficulty is that both primary and secondary inclusions may be present. The criticism of early temperature work on liquid inclusions is largely due to the non-

recognition by worker and critic of this latter fact.[1] Obviously if liquid inclusions have been formed secondarily within a mineral at one or more times after its crystallization, different observers' results will not check.

The material used in the present study presents neither of the two difficulties mentioned. Most of the sphalerite crystals used were the subhedral to euhedral ones formed in open cavities, such as the Tri-State district furnishes in abundance. Material of this type contains only primary inclusions.[2] Liquid and bubble only are present. The bubble's size, so far as observed, is always in ratio to the size of the enclosing cavity within a single crystal or within similar sphalerite crystals from a single locality. No exception was noted in the thousands of liquid inclusions observed during the work on which this paper is based.

In the heating experiments under the microscope, the bubbles in several similar-sized inclusions, in the same fragment of sphalerite, all disappear at the same temperature. Smaller bubbles in smaller cavities disappear (with the same magnification) some degrees lower than the larger ones in the larger cavities, because of the limit of microscopic resolving power. For close-temperature comparison of these, the magnification should be adjusted so as to give similar-sized images. It is considered that the liquid cavities were completely filled by solution (one phase) at the time of the formation of the sphalerite crystals. The apparent constant ratio of bubble size to cavity size within single crystals indicates that this is true. These liquid inclusions are doubtless composed mainly of an aqueous solution of NaCl.[3]

At the lower temperature ranges in which this work was done, the compressibility of water and presumably of concentrated sodium chloride solutions is so small that it may be neglected.[4] Its effect would be to raise slightly the apparent temperatures ob-

[1] Newhouse, W. H.: The Composition of Vein Solutions as Shown by Liquid Inclusions in Minerals. ECON. GEOL., vol. 27, pp. 421–422, 1932.

[2] *Op. cit.*, pp. 421–422.

[3] *Op. cit.*, pp. 428–436.

[4] Bowen, N. L.: Geologic Thermometry. Laboratory Investigation of Ores by Fairbanks, pp. 192–193, McGraw-Hill, 1928.

tained by this method. Due to the fact just mentioned and also to the limitations of microscope resolvability, the temperatures obtained are minimum temperatures, but probably only a few degrees less than the true ones.

Method of Examination.—Cleavage flakes or polished thin sections of sphalerite were examined under the microscope for inclusions. A polished smooth surface is necessary due to the high index of refraction of sphalerite. This is probably why the inclusions have not been widely noticed before. The thickness of the flakes or sections which may be used is dependent upon transparency. The inclusions may be readily seen in flakes 3–4 mm. thick in sphalerite from Santander, Spain. The thinnest sections used were about 0.5 mm. thick, of dark sphalerite. The thicker the sections that can be used the better, for more searching ground is available, and larger inclusions are more apt to be untapped in preparing the section. The size of the inclusions tested ranged from about 0.05 mm. to 0.5 mm. in maximum dimension. A strong light source is essential.

The chips or sections containing inclusions were observed in a variable temperature bath on a microscope stage.[5] A pyrex container shaped like an evaporating dish was insulated below and on the sides by asbestos paper to cut down convection currents and prevent damage to the microscope. A circular resistance coil within a glass tube was placed in the dish in a bath of paraffine or Crisco. The latter smokes less at higher temperatures. A mercury thermometer was placed directly in the bath.

The temperature was then raised until the bubble disappeared and temperature readings taken. This was done several times on each specimen, the observations being made some seconds after turning off the heat source. It could be seen by the microscope that the convection currents in the bath died down in this interval. A check with another thermometer showed the temperature readings as being 1°–3° in error. When the specimen is heated above the temperature at which the bubble disappears,

[5] Holden, E. F.: The Cause of Color in Smoky Quartz and Amethyst. Am. Min., vol. 10, pp. 215–218 (1925).

due to an undercooling phenomenon, it may not reappear for some degrees below the temperature of bubble disappearance. For large inclusions this undercooling may be only a few degrees, for small ones as much as 20° to 30°. The bubble then reappears in large size, with explosive suddenness. In a large inclusion six to twelve bubbles may simultaneously explode into view. These usually appear mainly in a ring concentric with the periphery of the inclusion. Evidently an inclusion filled with liquid must cool until sufficient energy is present to form the surface film before the bubble appears. It has been suggested [6] to the writer that little dissolved gas is present in the inclusions. If dissolved gas was present, on undercooling the liquid, the bubbles would probably appear simultaneously throughout the body of the liquid. In the absence of dissolved gas the bubbles should appear at the periphery of the cavity.

Discussion of Results:—The temperatures obtained for the deposition of the sphalerite from the various localities harmonize with the known data on associated mineralization and paragenetic relations. The Joplin and Picher sphalerite show temperatures of formation slightly higher than the Granby sphalerite which occurs with barite. The ruby blende from Joplin, one of the very latest minerals in the succession, also shows a lower formation temperature.

The mineralization in the lead-zinc region of Wisconsin and Illinois is suggestive of a lower temperature of deposition than that at Joplin, Mo. The former place shows finer depositional banding than in the Joplin region, and more commonly approaches colloform structures. The crystal size in openings and particularly in massive ore is in general smaller in the upper Mississippi Valley ores. Apparently also there is, in general, more lead present in proportion to the zinc in the Wisconsin-Illinois region. The removal of much zinc in the oxidized zone in this region makes the latter point uncertain. The Southeastern Missouri deposits show a still higher ratio of lead to zinc.

[6] Oral Communication, L. J. Gillespie, Professor of Physico-Chemical Research at Mass. Inst. Tech.

TEMPERATURE OF FORMATION OF SPHALERITE AS DETERMINED BY LIQUID INCLUSIONS.

Locality.	Remarks.	Temperature.
Joplin, Mo.	Dark brown crystals from cavities. Also "Pebble Jack."	125°–135° C.
Picher, Okla.	Dark brown crystals from cavities.	125°–130° C.
Tuckahoe, Mo.	"Pebble Jack."	115°–125° C.
Granby, Mo.	Massive coarsely crystalline dark brown sphalerite with barite.	110°–115° C.
Joplin, Mo.	"Ruby blende," well formed crystals resting on chert.	90°–105° C.
Boston-Kentucky Mine, Lockport, Henry Co., Ky.	Barite, sphalerite, galena vein, one spec. only. Massive dark yellow-brown.	70°– 95° C.
Badger Mine, Hazel Green, Wisc.	Dark brown, massive with Pyrite-Marcasite mixture.	80°–100° C.
Wisconsin	Banded ore, mainly dark brown sphalerite, minor galena.	90°–105° C.
Southeastern Missouri	Massive yellow sphalerite with one-half inch cleavage surfaces (one spec. only).	105°–125° C.
Picos de Europa, Santander, Spain	One subhedral crystal, evidently from cavity, also large cleavage fragments, some yellow, some light brown, quite transparent.	145°–160° C.
Rabenstein, South Tyrol	Well formed yellow and brown crystals, quite transparent.	145°–150° C.
Schemnitz, Hungary	Color growth zoned well-formed crystal. Incls. in greenish-yellow outer zone. Large incls.	180°–190° C.
Echigo, Japan	Well formed very dark brown to black crystal.	Bubbles still remain at 225° C.; estimated deposition temp. 250°–275° C.

The writer relates the higher temperature of deposition in the Southeastern Missouri ores to their replacement character, whereas the upper Mississippi Valley ores largely formed as fillings in open cavities. The galena in Southeastern Missouri may well have formed at a lower temperature than the sphalerite.

The low temperature of deposition of sphalerite in the barite vein from Lockport, Kentucky, is in harmony with previously known facts on barite mineralization. At Rabenstein the mineralization includes breunerite, pyrite, sphalerite, silver-bearing galena, barite, and a little chalcopyrite and polybasite.[7]

The mineralization at Schemnitz includes fine-grained quartz and amethyst, calcite, ankerite, rhodochrosite, rhodonite, siderite, barite, with much pyrite, galena, chalcopyrite, and sphalerite.[8]

Conclusions.

A ready means is now known by which the temperature of deposition of sphalerite may be determined. Since sphalerite is common in ore bodies, the method has wide application.

The ores of the Mississippi Valley lead-zinc deposits were formed by thermal solutions. The main deposition in the Tri-State district took place between 115° and 135° C., in the Upper Mississippi Valley region between 80° and 105° C.

Probably but little dissolved gas was present in the solutions when the sphalerite was deposited. More correctly, none has apparently been left after crystallization of the sphalerite.

The meager data suggest that areal temperature zoning is present in the Joplin region. This is in harmony with the conclusions of Emmons and the results obtained by Fowler.

By close temperature control of apparatus and by using a long focus microscope with high magnification, it should be possible by this method to determine readily temperature zoning in lead-zinc deposits of the Mississippi Valley as well as elsewhere. Successive generations of sphalerite in a deposit can be used to determine the temperature change in the ore-forming solutions. For close comparison from place to place, account should be taken of the size of cavity and resolving power of the microscope.

Free growing, well formed crystals of sphalerite, which were formed in openings, furnish ideal material for such temperature determinations. Massive sphalerite, which on thorough search

[7] Tornquist, A.: Metall und Erz, *26*, pp. 242–243 (1929).

[8] Lindgren, W.: Mineral Deposits, p. 581 (1928).

shows only one ratio of bubble size to cavity, is believed to be common, and to furnish trustworthy results where proper precautions are observed. Workers who deal with such material should familiarize themselves with previous literature on the subject, since the arrangement and character of the inclusions has a strong bearing on their origin as primary or secondary.

LABORATORY OF ECONOMIC GEOLOGY,
MASS. INST. TECHNOLOGY,
CAMBRIDGE, MASS.

CATALYSIS AND ITS BEARING ON ORIGIN OF LAKE SUPERIOR IRON-BEARING FORMATIONS.

CARL ZAPFFE.

INTRODUCTION.

THIS paper treats of physico-chemical and bio-chemical precipitation of iron and manganese from solution in water and emphasizes the probability that minerals of iron and manganese in the Lake Superior iron-bearing formations may have been so precipitated. It has to do, not with the origin of those iron ores and manganiferous ores which are considered to be secondary, but with the host formation in which they occur.

Early theory looked to the land areas for the materials composing the iron formations, to a long cycle of weathering, followed by solution and transportation of the silica, iron, and manganese, in ground and run-off waters, and precipitation of them in the sea. Later studies disposed of this theory in the minds of some geologists, who look to rapid deposition of the iron-bearing formations from solutions escaping into the sea by direct igneous action.[1]

To all who have studied these unique formations it is apparent that they are non-clastic sedimentary rocks, but there is no agreement concerning the original source of the materials of which they were built, nor the manner in which the materials were brought into the seas and the agencies by which they were precipitated. Evidence is accumulating in support of precipitation by bio-chemical and physico-chemical processes of the type called catalysis. This paper contributes some observations which are the incidental fruits of a study of the municipal waters of Brainerd, Minnesota.

Inasmuch as iron and manganese are closely associated in the

[1] Van Hise, C. R., and Leith, C. K.: The Geology of the Lake Superior Region. U. S. Geol. Surv. Mon. 52, p. 499 et seq., 1911.

iron formations, it has occurred to me that their occurrence in ground water, the rapidity with which they come out of solution in water mains, and the catalytic effect of the oxide of the one on the deposition of the other, would be of interest to a consideration of the depositional processes resulting in manganiferous iron formations like those of the Lake Superior region, or the deposits of iron and manganese in clay of the type occurring in the Cartersville District, of Georgia, and similar ones elsewhere.

The occurrence of manganese in the Lake Superior iron formations has not heretofore been considered of significance in relation to their origin and manner of deposition. As a matter of fact, until recent years manganese as a constituent of ground waters, although noted here and there, has received little study by geologists. Knowledge has been derived almost solely from studies of municipal waters in localities where manganese was discovered to be a nuisance in obstructing water mains, meters, and similar appurtenances. A few paragraphs will show what had been learned by other investigators prior to our studies at Brainerd.

IRON AND MANGANESE IN UNDERGROUND WATERS.

Water containing iron in amounts ranging between 10 and 15 parts per million is not an unusual occurrence; but for municipal purposes such waters are avoided, which accounts for the fact that published analyses are principally of waters that are in daily use. Available analyses for manganese rarely show more than 5 or 6 p.p.m.; but inasmuch as analyses are not often made for manganese, it is probable that higher contents are not unusual and that it occurs in the waters of many localities of which analyses have not been made.

Europe supplies more information about manganese in water than does this continent, few analyses being reported for the United States prior to 1911. Among the first in the United States to study a municipal water system for manganese was Jackson [2] who in 1901 reported 1.4 p.p.m. as the manganese-con-

[2] Jackson, D. D.: *Crenothrix manganifera* in Newton, Mass. Jour. Soc. Chem. Ind., 21, p. 681 et seq., 1901.

tent in the water of Newton, Mass. No areal survey was made until 1911, when Bartow [3] and Corson [4] collaborated and then separately discussed their findings as to manganese in waters from streams and wells in Illinois. They reported iron ranging between 1.00 and 51.2 p.p.m. and manganese up to 7.8 p.p.m. Sale [5] reported in 1917 that in Pierre, So. Dak., water containing 2.3 p.p.m. was being used. Montfort,[6] in 1926, stated that manganese is rarely absent from ground and surface waters, and reported as much as 4.5 p.p.m. in Excelsior Springs, Mo. Lathrop [7] stated in 1929 that the Ohio river, at Steubenville, contained 4.8 p.p.m. of manganese. In 1930 water from a well drilled in glacial drift near Ironton, Minn., was found by the writer to contain 146 p.p.m. of manganese and the supply for the village of Deerwood five miles away contained 1.10 p.p.m.

In Europe the search for manganese in water was pursued earlier and more vigorously than in the United States. For Arad, Hungary, Hajeck [8] describes troubles with precipitates arising in 1896, but that manganese was involved in the precipitates remained undetected until 1903. At the same time Weibull [9] recognized manganese in deposits in streams and ponds on the Bjornstorp estate in Sweden and found manganese in four wells, one well containing as much as 13 p.p.m. In 1913 Schmeitzner [10] discussed manganese in waters in Germany and also commented on contents of iron up to 100 p.p.m. During the last several

[3] Bartow, E.: Occurrence of Manganese in the Water Supply and in an Incrustation in the Water Mains at Mt. Vernon, Ill. Univ. of Ill. Bull., vol. 10, no. 36, Ser. 10, pp. 57–65, 1913.

[4] Corson, H. P.: Manganese in Water Supplies. Univ. of Ill. Bull., vol. 14, no. 5, pp. 144–204, 1916.

[5] Sale, J. W.: Manganese in Water Supply of Pierre, So. Dak. Engin. News Record, Feb. 2, 1917.

[6] Montfort, W. F.: Water Works, pp. 169–172, 1926.

[7] Lathrop: Water Purification Problems in Ohio. W. Va. Univ., Coll. of Eng., Bull. 2, p. 18, 1929.

[8] Hajeck, R. H.: Gelungene Ausscheidung der Manganverbindung aus Tiefbrunnenwasser. Jour. Gasbel. u. Wasserfach., vol. 33, 767; 8/18/07.

[9] Weibull, M.: Ein Manganhaltiges Wasser u. eine Bildung von Braunstein bei Bjornstorp in Schweden. Zeit. für Nahr. u. Genus., Bd. 14, 403–5, 1907.

[10] Schmeitzner, Dr. R. von: Ueber Entmangung von Trinkwasser. Tech. Gemeindeblatt, vol. 15, no. 21, 343, 1913.

years it has been discovered that manganese in small amounts in municipal water is far more objectionable than iron in large amounts, and the author,[11] writing in 1929 and 1931, has shown that the problems arising from the presence of manganese in such waters are now receiving some attention in this country.

Although the element, manganese, was discovered in 1774, it was not reported in underground water until 1896 and that discovery was hardly noticed until the Breslau calamity in 1906, to which reference is made below. Molisch [12] was the first to detect spots of manganese on thread bacteria and cocci, in Germany in 1892; and not until 1901 did Jackson [13] discover accumulations of manganese on a thread bacteria in the United States. At the time little attention was paid to these observations because manganese in potable water, as Jackson said, was then considered a rare occurrence. Manganese in municipal water did not receive serious attention even in Europe until 1906, when the supply of Breslau, Germany, was endangered by floods in the valley of the river Oder,[14] during which the manganese in the wells rose to 231 p.p.m. and the iron to 372 p.p.m.,[15] although in European cities manganese had been recognized definitely since 1904 [16] as a substance responsible for the clogging of water pipes.

Soil bacteria,[17] universally present in abundance, as well as inorganic chemical action, create soluble forms of iron and manganese, which explains why ground waters commonly contain

[11] Zapffe, Carl: (*a*) Elimination of Manganese from Ground Waters. Minnesota Municipalities, vol. XIV, no. 9, Sept. 1929. (*b*) Deposition of Manganese. Econ. Geol., vol. 26, no. 8, pp. 799–825, 1931.

[12] Molisch, H.: Die Eisenbakterien. Centralb. für Bact., Abt. 2, Bd. 29, 241–243, Jena, 1911.

[13] Jackson, D. D.: *Op. cit.*

[14] Lührig, H., and Blasky, A.: Mangan im Grundwasser der Breslauer Wasserleitung und die Frage der Abscheidung des Mangan sulfates aus demselben. Chem. Ztg., 31, 255–57, 1907.

[15] Beyschlag, F., and Michael, R.: Ueber die Grundwasserverhältnisse der Stadt Breslau. Zeit. Prakt. Geol., vol. 15, 153–164, 1907.

[16] Schorler, B.: Die Rostbildung in den Wasserleitungsröhre: Centralb. für Bact., Abt. II, Bd. 15, 564–68, 1906.

[17] Waksman, S. A.: Principles of Soil Microbiology. Williams & Wilkins Co., Baltimore, 1927.

these salts in quantities far in excess of what is deemed permissible in water supplies.

The City of Brainerd, Minn., obtains its water from gravel beds in the glacial drift. During the past ten years the daily average content of iron has been 1.2 p.p.m. and of manganese 0.8 p.p.m., with maxima of 3.0 and 1.5 respectively. The city has experienced much trouble from precipitation of both iron and manganese in the street mains. Water supplies in cities of neighboring states with contents of iron and manganese up to 4 p.p.m. have lately been reported to the writer by plant operators. Occurrences such as these are not to be regarded as exceptional.

It is now clear that iron and manganese in fairly large amounts are normally present together in surface and underground waters in many localities. For reasons yet unknown, they are occasionally present in water and drainage systems in amounts vastly in excess of the normal as, for illustration, the Oder and Elbe rivers in Europe, which at times are very high in iron, as shown by the experiences of Breslau, Dessau, Glogau, Dresden and other cities. Municipal waters have been rendered useless for a month at a time due to sudden increases in content of iron; many instances of this in France, Germany, Holland, and England are on record even as far back as 1870. Ellis [18] says that a number of European cities, in 1870 and later, were in desperate circumstances because of sudden heavy increases of iron in their water supply accompanied by abnormal development of bacteria, rendering the water foul in odor and taste and red or brown in color.

One part per million is only 1/10,000th of one per cent., but from one million gallons of water per day with that amount of iron or manganese in it can be deposited two tons of ferric or manganese oxides per year. When it is considered that one million gallons can be pumped from a few small wells in a few hours, it is apparent that the run-off waters of a drainage basin containing a numerically minute quantity of iron and manganese in solution actually transports an enormous tonnage of these elements in a few thousand years. Therefore it is natural that a witness to the rapid deposition of iron and manganese in a mu-

[18] Ellis, D.: Iron Bacteria. Methuen & Co., Ltd., London, 1919.

nicipal water system is not willing to grant the unimportance of weathering, transportation, and deposition in the accumulation of these elements in natural formations.

CHEMICAL REACTIONS AFFECTING IRON AND MANGANESE IN GROUND WATERS.

Water chemists now believe that iron and manganese in solution in surface or ground waters are mainly in the bicarbonate form and that even in waters in which other compounds predominate some bicarbonate is always present.

Deposition of iron and manganese oxides is commonly brought about through bacterial action in conjunction with catalysis. Deposition can be accomplished by bacteria alone, but it so happens in nature that if bacteria are active, catalysis is brought into play by the oxides of manganese and iron formed by them. Bacteria supplement as well as aid and expedite deposition by inorganic reactions.

Even if only a little manganese bicarbonate is present with other salts, such as the sulphate or carbonate, in preponderance, manganese dioxide is inevitably formed from the more readily dissociated bicarbonate, mostly by bacterial action. The oxide once formed, the other manganese compounds are disrupted by catalysis and go down as oxides. Ferrous sulphate and iron bicarbonate are oxidized in the same manner, *i.e.* through the catalytic influence of manganese dioxide, or manganese dioxide mixed with ferric oxide, although under some conditions precipitation of iron oxides results simply through contact with the oxygen of the atmosphere.

In 1885 Dieulafait [19] discovered that when one of several reactions takes place, the first to occur is that one which is attended by the greatest evolution of heat. Consequently, if MnO and FeO are both present and CO_2 is available, not only will manganese carbonate form first but it will also be the more stable. If O and CO_2 act together in considerable excess, Fe_2O_3 and MnO_2 will be formed; but if they are present in small quantities and act slowly, then the oxygen will unite with the iron to form Fe_2O_3

[19] Dieulafait, L.: Compt. Rend., vol. 101; pp. 609, 644, 676; 1885. Clarke, F. W.: Geochemistry. U. S. Geol. Survey Bull. 770, 5th ed., 1922.

and the carbon dioxide will unite with the manganese to form $MnCO_3$, because in this instance the reaction with the iron generates the greater heat, to wit:

(1) $FeO + CO_2 = FeCO_3 + 5.0$ calories
$MnO + CO_2 = MnCO_3 + 6.8$ "
(2) $2FeO + O = Fe_2O_3 + 26.6$ "
$2MnO + 2O = 2MnO_2 + 21.4$ "

According to those principles, if oxygen is available in adequate amount, the oxides of both metals will be formed, otherwise stable carbonates will form.

The following reactions for oxidation of iron and manganese bicarbonates have been developed by Tillmans [20] from his experiments in connection with municipal water supplies of Germany:

(1) $2Fe(HCO_3)_2 + H_2O + O = 2Fe(OH)_3 + 4CO_2$
or $Fe_2O_3.3H_2O + 4CO_2$
or $Fe_2O_3.nH_2O + H_2O + 4CO_2$

(2) (*a*) $Mn(HCO_3)_2 + H_2O = Mn(OH)_2 + 2H_2CO_3$
(*b*) $2Mn(OH)_2 + O = 2(MnO.OH) + H_2O$
or $Mn(OH)_4$
or $MnO_2.2H_2O$

Weston [21] showed by experiment that ground water percolating through glacial drift and rock formations dissolves iron and manganese, mostly as bicarbonates but in part as sulphates. He also found that water falling only a few inches through air absorbs much oxygen, as follows:

Amount of Fall	p.p.m. of Oxygen Absorbed
4 inches	4.0
10 inches	5.0
20 inches	5.75
80 inches	10.57

[20] Tillmans, Dr. J. von: Über die Entmanganung von Trinkwasser. Jour. für Gasbeleuchtung, München, vol. 57, 713–24, 1914. Tillmans, J., Hirsch, P., and Grohman, H.: The Physical Chemistry of Demanganization of Drinking Water. Gas- und Wasserfash, Munich, I, II, III, 1928.

[21] Weston, R. S.: Some Recent Experiences in the Deferrization and Demanganization of Water. Jour. N. E. Water Work Ass'n., 28, 27–59, 1914.

and that 1 p.p.m. of oxygen will oxidize as much as 7 p.p.m. of iron. Brown,[22] working with waters near London, England, concluded in 1904 that ground water upon reaching the surface dissolves oxygen quickly and to the extent of six volumes per thousand; a few miles from the pumping station he found the water in the mains saturated with oxygen. Ground water occludes oxygen when it reaches the surface and contacts the atmosphere. Surface waters manifestly are always contacting atmosphere and, therefore, occlude oxygen in large amounts. Moberg [23] found that in the Pacific ocean the surface water is nearly saturated with oxygen, that oxygen decreases from the surface to about 2000 feet, where 1 p.p.m. was found, and that farther downward it increases to the bottom. The highest deep-water oxygen content was found by him to be 3.45 parts per thousand of water.

Thread bacteria are in general much alike but differ in special respects. Some are more abundant in waters that are stale or stagnant and others, in waters that are purer. All are endowed with a capacity for absorbing large quantities of carbon from the bicarbonate of iron and most of them from the bicarbonate of manganese. The carbon is their food. They are alike in that all require the presence of oxygen. This oxygen forms insoluble oxides of the iron and manganese radicles that are the residues from the bacterial disruption of the bicarbonates and those that result from oxidation by catalysis. The presence of oxygen is to be expected in ground and surface waters in quantities sufficient to satisfy iron and manganese, even if present in far more than normal amounts.

Sampling of surface- and well-waters has not usually been done in a way to afford analyses that reflect satisfactorily the average content of iron and manganese. Samples from the top layers of a stream, lake, or storage reservoir are not representative; neither are samples taken only from water taps in homes. The author [24] has shown that the contents of iron and manganese vary in dif-

[22] Brown, J. C.: Deposits in Pipes and Other Channels Conveying Potable Waters. Proc. Inst. Civil Engrs., vol. 157, pt. 2, pp. 1–17, London, 1904.

[23] Moberg, E. G.: Science Supplement, vol. 73, no. 1892, April 3, 1931.

[24] *Op. cit.*

ferent parts of a body or stream of water. Weston [25] found marked differences in the content of manganese in the various layers of a storage reservoir 77 feet deep. These metals are repeatedly dropped in moving water and again taken into solution, and this must be taken into account in proper sampling. Moore and Maynard [26] state that in rivers conditions may be such that large quantities of iron are carried in colloidal form, depending on organic matter present. Raumer [27] and Weston [28] stated that iron is held in solution by organic matter, and, as Weston further said, by the presence of carbon dioxide or by manganese; Weston found also that if iron goes down, it will be taken up again by manganese if the manganese does not go down with the iron.

Baylis [29] showed that certain filter sands, used in Baltimore, had accumulated a coating of slimy bacterial growth which, when submerged in water for a week or so, gave the water a content of as much as 10 p.p.m. of manganese. A few species of bacteria produce acids that will dissolve manganese, and apparently the coating of manganese on these sands is made redissolvable through the action of bacteria. Kühr,[30] working with the water system at Leiduin, Holland (dune waters), says that in anerobic processes undissolved manganic compounds can pass into dissolved compounds and that dissolved manganous compounds can be transformed into undissolved manganic compounds through the agency of bacteria—a biologic oxidation process. The bacteria found there were of a lower order than thread bacteria. Janzig and Montbank,[31] working with filter sands of the Minne-

[25] Weston, R. S.: Manganese in Water—Its Occurrence and Removal. Water Works and Sewage, LXXVIII, no. 7, 196–8, 1931.

[26] Moore, E. S., and Maynard, J. E.: Solution, Transportation and Precipitation of Iron and Silica. Econ. Geol., Parts I–III, vol. 24, nos. 3, 4 and 5, 1929.

[27] Raumer, E.: Über das Auftreten von Eisen und Mangan in Wasserleitungswasser. Zeit. für Anal. Chemic. 42, 591–602, 1903.

[28] Weston, R. S.: *Op. cit.* Note 21.

[29] Baylis, J. R.: Manganese in Baltimore Water Supply. Amer. W. W. Jour., vol. XII, 211, 1924.

[30] Kühr, C. A. H. von. Wolzogen: Manganese in Water Works. Amer. W. W. Ass'n., vol. 18, no. 1, July, 1927.

[31] Janzig, A. C., and Montbank, I. A.: High Manganese Effluents from Idle Filters. Jour. Amer. W. W. Ass'n., vol. 21, no. 10, October, 1929.

apolis, Minn., filtration plant, using Mississippi river water, found that precipitated manganese oxide was redissolved under conditions of stagnancy, and that biologic action, fostered by anerobic conditions, was an important factor in the reaction. Most of these observations are very recent.

THE EXPERIMENTS AT BRAINERD.

During 1928, 1929 and 1930 the writer initiated and personally conducted tests in a pilot plant for the City of Brainerd, Minnesota, to discover a method for removing manganese from the municipal water supply. Attempts had been made in Germany since 1906 and in the United States since 1914 to accomplish removal of manganese, but total elimination was never attained. In Dresden, Germany, manganese was removed [32] by using bacteria on the sand filters, but in water containing 0.65 p.p.m. only a portion of it was precipitated. According to Harder [33] water must contain as much as 0.2 p.p.m. of iron, or manganese, in order to foster the propagation of thread bacteria. It appears, therefore, that bacteria alone are effective in waters for which the iron and/or manganese ranges between 0.2 p.p.m. and less than 0.65 p.p.m.

Considering that nature, unassisted by any chemicals introduced into the Brainerd water, was precipitating rapidly in the mains all of the manganese, experiments were devised to duplicate these natural conditions above ground in order to precipitate the manganese (and iron) before the water was put into the mains. An important matter that had to be determined was to what extent thread bacteria, whose favored habitat for propagation is water mains, were functioning; and if so, were they essential to inorganic processes, if any, that were operating simultaneously. Both ærobic and anerobic conditions exist in different parts of a water system, and whatever transpires there is probably duplicated in nature over and over again in all sorts of places. A water

[32] Vollmer, D.: Die Entmanganung des Grundwassers im Elbethal und die für Dresden Ausgeführte Anlagen. Jour. Gasbel. u. Wasserversorgung, vol. 57, no. 43–44, pp. 940–8, 956–9, 1914.

[33] Harder, E. C.: Iron Depositing Bacteria and Their Geologic Relations. U. S. Geol. Survey Prof. Paper 113, 1919.

system is merely a means of confining flowing water to certain channels.

Precipitates that were collected for study from different parts of the Brainerd distribution system contain 30 per cent. or more manganese (dried at 212° F.) and up to 15 per cent. iron, with silica ranging from 6 to 8 per cent. These precipitates, when still soft and muddy, exhibit an abundance of *Crenothrix polyspora* (Cohn), *Leptothrix ochracea* (Kützing), *Gallionella ferrugineum* (Ehrenberg) and *Spirophyllum ferruginea* (Ellis). These bacteria occur also in the precipitate that settles in the closed collecting reservoir at the wells, but this precipitate was found to contain 33 per cent. in iron and only 7 per cent. in manganese. In other words, manganese is two to three times more abundant in the mains than iron, whereas in the water in the wells constituting the source the iron is more abundant than manganese and the manganese which separates from the water in the closed storage reservoir at the wells is less than that from the water in the mains. Strangely, these same relations, both as to amounts and places of deposition, are the same in Brainerd as they were found to be in several European localities. These relationships are, therefore, not local. They are shown in Table I.

Manganese, it was found, is precipitated in the mains rapidly and eventually completely, the speed of the reaction suggesting

TABLE I

MANGANESE AND IRON IN BRAINERD WATER.

	Water at the Source p.p.m.	Natural Precipitates		
		In Collecting Reservoir (before reaching mains). %	In Mains. %	In Meter. %
Fe	1.2 to 2.0	33.3	13.3 to 18.5	11.2
Mn	.8 – 1.2	7.1	29.0 – 33.0	33.0
SiO_2	13.0 – 15.7	11.9	5.5 – 7.1	4.7
CaO	80.8 – 90.8	4.1	1.8 – 5.6	?
MgO	18.8 – 29.3	0.5	0.3 – 2.9	?
Al_2O_3	0.6 – 2.6	?	0.4 – 0.7	?
Loss on ignition		?	18.0 – 23.5	?
P		?	? ?	0.13

that some process other than bio-chemical is in operation. The iron content of the water in the mains first decreases as the water leaves the pumping station and then increases with distance from the pumping station, suggesting that the precipitated iron is redissolved and reprecipitated in that section of the distribution system which is between the source of supply and the consumer's tap. The quantity of material deposited in the collecting reservoir at the wells is small. In the mains the quantity is large and the silica-content of it is here very small compared to the quantity in solution at the source. Weibull [34] found the same in Sweden; water containing 30 p.p.m. of silica when left standing for two months in a closed jar deposited only 4 parts of the 30 parts.

When slightly alkaline source-water was thoroughly mixed with the precipitate taken from the mains and filtered, all manganese and iron separated quickly as oxides. The water in the Brainerd mains is slightly alkaline and oxidizing. In the mains the precipitation of manganese dioxide was presumably started by bacterial action, but the precipitate formed by bacteria exerts a remarkable catalytic influence on the compounds of manganese and iron in solution, accelerating their deposition independent of bacteria until the process is complete. By catalysis, the bicarbonate of manganese is first broken up into carbon dioxide and manganous hydroxide, and the latter is eventually converted into manganic hydroxide and manganese dioxide.

It has been demonstrated by Molisch,[35] and others, that the sheaths of the bacteria are alkaline; and being also mucilaginous, they hold the manganese radicle until oxygen in the moving water is available in amount to form the stable oxides from the unstable manganous compounds. Ellis says the organism exudes an enzyme which oxidizes catalytically. Alkalinity is essential to these manganese reactions; Binz [36] in 1901 and Adler [37] in 1914

[34] *Op. cit.*

[35] Molisch, H.: Die Eisenbakterien. Centralb. für Bakterien, Abt. 2, Bd. 29, 241–243. Jena, 1911.

[36] Binz, C.: Deutsche Medizinische Wochenschrift, no. 14, p. 219, 1901.

[37] Adler, O.: Über Eisenbakterien in ihrer Beziehungen zu den therepeutisch verwendeten natürlichen Eisenwässern. Centralb. f. Bakteriologie, Abt. 2, Bd. 9, 215–19, 277–87. Jena, 1914.

demonstrated that a relationship existed between alkaline reactions in water from which iron was being precipitated and the alkalinity caused by certain bacteria and algæ. Tillmans [38] concluded in 1914 that bacteria produce the alkalinity needed for the reaction.

Alkalinity is not essential to the precipitation of iron oxides from iron bicarbonate by simple aeration. But simple aeration alone will not precipitate manganese oxides from the manganese bicarbonate, with or without the presence of iron carbonate. Emmons [39] said in 1917 that lime and oxygen must be simultaneously applied or else manganese remains in solution; and that water passing through limestone alone readily removes iron but not manganese.

In the presence of manganese dioxide, no matter how formed, or an enzyme produced by bacteria, iron and manganese bicarbonates are rapidly broken up and the iron and manganese are precipitated as hydroxides or oxides. It has been demonstrated that manganese dioxide plus a little ferric oxide constitutes a more powerful catalytic agent than manganese dioxide alone.[40]

Oxidation by aeration can be accomplished in many ways. Methods employed in removal plants are but duplications of nature's most attractive displays, like spraying, plunging, cataracting and splashing. In some plants, air was pumped into the water, and in others the water was made to flow over broken stone or through submerged beds of stone or coke. In some plants aeration is accomplished by trickling the water through limestone, or marble, or crushed lava, or crushed porphyry, which procedure also fosters alkalinity.

Water from the Brainerd wells, if kept in jars placed on a window shelf, will in thirty minutes become opalescent-cloudy from the finely divided silica that separates. It gradually settles

[38] Tillmans, J.: Ueber die Entmanganung von Trinkwasser. *Op. cit.*

[39] Emmons, W. H.: Secondary Enrichment of Ore Deposits. U. S. Geol. Surv. Bull. 625, pp. 438–9, 1917.

[40] Falk, Geo. K.: Catalytic Action. Chem. Cat. Co., New York, 1922. Rideal, E. K., and Taylor, H. S.: Catalysis in Theory and Practice. MacMillan & Co., Ltd., London, 1926. Hilditch, T. P.: Catalytic Processes in Applied Chemistry. D. Van Nostrand Co., New York, 1929.

at the bottom. Whether the jars are left open or closed, the iron does not oxidize and settle until after two or three days have elapsed. The precipitated iron is mostly gelatinous and on settling does not seem to commingle with the silica layer. In jars left open, a few small granules of oxides form and sink into the layer of silica on the bottom. Brainerd water contains 14 to 15 p.p.m. of silica, but in the precipitates in the mains, where iron and manganese analyze very high, silica analyzes only 5 to 7 per cent. This relation as to silica deposition has been found also in Europe. The Brainerd water is high in the bicarbonates of calcium and magnesium; Moore and Maynard [41] say that calcium and magnesium bicarbonates are nature's two best solvents of silica. Perhaps silica is thus kept from precipitating in the mains. Sodium bicarbonate is not abundant in waters in this region.

SUMMARY.

It has been emphasized that run-off and ground waters carry important amounts of silica, iron and manganese in solution. These are the important constituents of the Lake Superior iron formations. It has been shown that iron and manganese are dependent in their chemical reactions on changing conditions in any solution in which they occur, and the processes through which they may be precipitated from solution have been described. It has been observed that they occur in underground and run-off waters mainly as bicarbonate; that from such waters iron may be precipitated by simple aeration, but not manganese, and not all of the iron in the presence of manganese; that manganese may be precipitated as oxides if the solutions be slightly alkaline and contain plenty of free oxygen, and iron may be precipitated if the solution is a bit acid; that oxidation of the solutes can be started by bacteria of several kinds, but whether started by them or other means the process is greatly accelerated by the catalytic influence of the oxides, especially the dioxide of manganese; and finally, that if the solution is highly charged with carbon dioxide, stable carbonate of iron and manganese will form. In all the processes

[41] *Op. cit.*

certain bacteria exert a strong influence on precipitation, which is subordinate, however, to the catalytic action of the oxides, no matter how formed or how introduced. This power of catalysis by pyrolusite on manganese bicarbonate in water was not clearly recognized prior to 1912, when Poppel [42] experimented with pyrolusite and chalk, although Gans and Lührig, when experimenting in 1909, after the Breslau calamity previously referred to, observed such deposition when pyrolusite was sprinkled on top of sand filters.

By taking advantage of these simple principles we have built in the City of Brainerd, Minnesota, a demanganization and deferrization plant of one and one-half million gallons per day capacity. For more than a year we have been easily, simply and quickly eliminating all iron and manganese from the water before it reaches the mains. No operators and virtually no supervision are needed. The plant takes advantage of the tremendous efficacy of catalysis, in this case mainly the catalytic action of manganese dioxide in the form of pyrolusite, acting on the soluble forms of manganese and iron occurring in the well-water. The oxides extracted from the water as precipitates are retained and enabled to function, as does the pyrolusite which is used to start the reaction. Bacteria are provided with an environment which is favorable to their assembling and propagating, thereby contributing their function before the water can enter the mains. Bacteria are especially important in providing the desired degree of alkalinity. Nature has been copied, nothing more.

Fig. 1 shows the Brainerd plant. Its design was influenced by the desire to effect cheapness and convenience of operation. To the reader it may seem that the city has not followed exactly the fundamental principles of the process as it functions in natural bodies of water but it should be understood that this plant was designed to enable each factor to function at the maximum of advantage and capacity, which explains why removal of manganese and iron is complete. This plant is a demonstration of the efficacy of catalysis operating under simple natural conditions.

[42] Poppel, A.: Entmanganung von Wasser. Chem. Ztg., 36, pt. 2, 1912.

APPLICATION TO PRECIPITATION OF IRON FORMATIONS OF THE LAKE SUPERIOR TYPE.

The origin of the manganese in the ore formations heretofore has been given very little consideration. Inasmuch as it occurs in large volume in association with the iron in the ores and has commercial value, it is surprising that so little study of it has been made. As a student of the geology of the Lake Superior region, the author naturally has sought to apply the facts and inferences growing out of his investigations at Brainerd to the problem of precipitation of the iron-bearing formations including

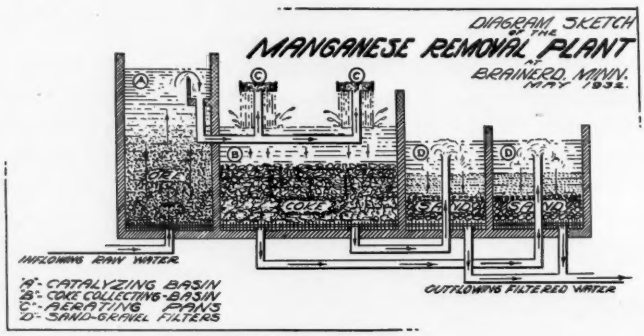

FIG. 1. Diagram of Brainerd plant.

both the manganiferous and the iron phases. Although the writer can not at this time undertake to develop this phase of the subject with any approach to completeness, he feels justified in making reference to a number of interesting considerations that point the way to further studies of this captivating and perplexing problem.

The principal iron formations of the region occur in the Middle and Upper Huronian, the ores mainly in the Middle Huronian. The Middle Huronian is now considered by most geologists to include the Biwabik formation of the Mesabi District long deemed Upper Huronian. The generalized Middle Huronian section is a coarse clastic—iron formation—slate tri-formational sequence

unassociated with extrusives. Igneous rocks of this period are overwhelmingly acid-intrusive and these are expressive of the orogenic revolution that brought the sedimentation to an end. The Upper Huronian group is a slate-graywacke formation, containing bands of iron-bearing formation, associated characteristically with basic extrusives.

Were these iron formations thrown down through the influence of organisms? Or by the physico-chemical phenomenon catalysis? Or by catalysis assisted by organisms? The answer is suggested by what has been related in the foregoing pages. Why could not these iron- and manganese-bearing formations have been deposited as similar materials are every day being deposited naturally in the gathering places between wells and mains, as at Brainerd? One deals there with only simple and natural laws, so simple that they have been put to practical use with dependable results.

(1) In considering the significance of the experiments at Brainerd, note first the composition of the natural precipitates in the water mains. Fairly complete analyses of these precipitates are at hand from which enough is known of their composition to indicate a striking similarity to a common type of manganese-bearing iron formation. The similarity is not confined merely to mineral compounds but extends also to their relative proportions. It is to be noted that the minerals in this precipitate are oxides; carbonates are few and silicates are lacking.

Until recently it was thought that all of the iron and manganese in these Huronian formations had been precipitated as carbonates and silicates. Opinion now inclines to the view that manganese and iron were precipitated largely as oxides. Space will not permit the discussion of this question, but attention may be called to the probability that under ordinary circumstances the tendency in open seas would favor the deposition of oxides. Recent study by Moberg of the oxygen-content of the Pacific ocean shows the very large amount of oxygen to be found at the surface and at great depths; and Dieulafait's work shows that when oxygen is present in excess of carbon dioxide, ferric and manganic oxides form as

long as the available supply of oxygen lasts. Only when the supply of oxygen becomes deficient do carbonates form.

Conditions in open seas are simulated by the Brainerd deferrization and demanganization plant, where an adequate amount of atmospheric oxygen is made available after catalysis to form oxides of iron and manganese to the exclusion of carbonates. Conversely, with oxygen deficient, oxide of iron is first formed and to the extent made possible by the quantity of oxygen present; thereafter the remaining iron and the manganese are converted to carbonates, manganese carbonate forming first.

(2) Not enough chemical work has been done to warrant the statement that the precipitates in the demanganization and deferrization plant are the same in every respect as those formed in the water mains. We know definitely that all of the iron and manganese in the water is deposited in the plant as oxides. We have not yet accurately determined all that happens to compounds of calcium, magnesium, aluminum and phosphorus in solution in the raw water. It is already indicated, and will be made known when certain studies in progress to confirm it are completed.

(3) Although the conditions in the water mains determine precipitation of the iron and manganese in oxide form, and in the plant as well, where the depositional processes of the mains are merely copied and perhaps hastened, it would be easy to establish and control conditions in both plant and mains whereunder the iron and the manganese would be precipitated as carbonates. This would involve merely prevention of contact of the raw water with oxygen and artificial provision of an excess of carbon dioxide.

(4) Inasmuch as conditions under which oxides on the one hand and carbonates on the other are deposited are now clear and well understood, it is not an abuse of the imagination to suppose that under natural conditions in open seas oxides may have been deposited in one phase and carbonates in the other; or that these two phases of deposition may have operated simultaneously in different parts of the deposition area. Finally, the conditions in a given area may oscillate rapidly from one phase to the other, just as variations in hydrogen ion concentration can determine

whether both iron and manganese are to be deposited or only iron. Inasmuch as it appears that the conditions that determine the oxide deposition are more dominant in open seas, it seems probable that much of the iron formation which is oxidized but unleached, as we see it now, is in that respect an original phase.

(5) It has been concluded, so far as known, by all geologists of the Lake Superior region, that ferrous silicate, in the form called greenalite, is an original mineral; and that in the Mesabi District particularly, greenalite is almost but not quite exclusively the original source of the oxides of iron. It is supposed to have been formed somewhat as glauconite is known to be formed, although it is not concretionary, like glauconite, in the sense that the grains have grown about a nucleus of foreign matter by successive accretions at the surface. No traces of such nuclei, if any there were, now remain; and the concretionary structure which is only here and there sparingly simulated seems to be secondary.

There is, however, nothing in the character of the mineral itself and in its mineralogical habitat to lead one to suppose that greenalite is necessarily original. On the contrary, there seem sound reasons for believing that the mineral greenalite and all other silicates in the iron formation are secondary. In the experiments at Brainerd, silica comes down in flocculent colloidal form if the water be allowed to stand quietly in contact with air; furthermore, it comes down before the iron begins to oxidize. Also, in all of the precipitates, silica is present as such and is uncombined with iron or manganese or the bases. Of course, no one would expect the deposition of silicates under those conditions, and no way is known in which oxides and carbonates may be thrown down simultaneously with silicates. It is obvious that the iron formations were deposited in open seas and probably under normal climatic ranges in temperatures and under moderate pressures not in excess of atmospheric pressure plus the weight of the water above the place of deposition. Under such conditions, oxidation, hydration and carbonation would occur, but I do not see how silication could operate at the same time to form ferrous silicate on a grand scale. The physical conditions controlling

silication are opposed to those controlling oxidation, hydration and carbonation and I am, therefore, unable to reconcile the deposition of ferrous silicate in company with the oxides and carbonates of iron and manganese.

All of the iron silicates in the iron-bearing formation, greenalite excepted, have been described and accepted as secondary —the products of anamorphism. Similarly, greenalite is considered, like the other iron silicates, secondary and a product of anamorphism. If it be so considered, the deposition of the iron-bearing formation presents nothing unusual or difficult of interpretation. Silica, its main constituent, went down as such; the iron and the manganese as hydrated oxides and carbonates; the lime and magnesia as carbonates; all in accordance with simple laws of chemistry and nothing in apparent contradiction with them. When the iron formations were buried by overlying sediments and later deformed or intruded, anamorphic changes took place, the extent and completeness of which varied from one locality to another in accordance with the anamorphic conditions, whether incipient, moderate or severe. The anamorphic changes were in the direction of dehydration, deoxidation, decarbonation and silication. All these principles are illustrated in the Biwabik formation of the Mesabi District.

The silica originally deposited had later on little else but iron to unite with, and thus formed ferrous silicate as a first step in anamorphism following burial. The globular structure of this silicate (greenalite) was all that this incipient anamorphic stage required of this mineral to accommodate it to the newly imposed conditions of burial with its consequent pressure. The iron silicate gruenerite, the iron-bearing amphiboles, garnets, staurolites and andalusite, to name just a few, are accepted indicators of intense anamorphism. So, from the west end to the east end of the Mesabi a progressive change takes place from incipient to advanced anamorphism resulting from conditions of burial. The more intense anamorphic changes at the east end are the consequence of the added loading of the large flows of gabbroid rocks. At that place the development of magnetite is on a large scale, whereas westwardly this development is not as pronounced but

presumably is in conformance with the degree of earlier burial in those westerly portions. The presence of this magnetite is evidence of de-oxidation; and its formation, even though sparing in certain places toward the west, probably indicates there a slight further advance from the incipient anamorphism that gave rise to the formation of greenalite. As anamorphism advanced in intensity it led to the development of minerals of crystal shapes suitable to the degree of burial, weight and distortion to which the formation was being subjected. The lack of angular shapes for the greenalite need raise no more question about it than that the greenalite be accorded its place in the anamorphic scale. Thereby one not only conforms to all the fundamental principles of metamorphism but one follows the simplest laws of chemistry and physics and does not wander in a maze of unrealities to the neglect of physical conditions that are perfectly obvious.

(6) The investigations at Brainerd and more or less similar ones in Europe, to which reference has been made herein, add little to the solution of the question of whence and in what manner came the materials of the iron formation into the sea. These materials are in solution today in ground waters and run-off waters, and attention has been called to the peculiar and inexplainable fact that the quantity of iron and manganese carried by some rivers is at certain times enormously augmented. We are not convinced from existing data that the accepted and ordinary processes of erosion and transportation account satisfactorily for the accumulation of these unique formations. This feature of the subject has been studied by Van Hise and Leith who, in 1911, concluded that such processes, so far as then understood, were inadequate. They thereupon advanced the theory that by direct igneous action these materials may have been contributed to the seas in whole or in part from basic submarine flows. They regarded the theory as highly speculative. Speculations on this phase of the subject are not apt to be confined to this generation of geologists. The present does not always seem to be a key to the past, with acknowledgments to the general usefulness of Hutton's great principle. Formations of this kind are apparently confined to the pre-Cambrian but they occur in all present climatic

zones. It may well be that they are to be accounted for by a combination of certain physico-chemical phenomena and atmospheric and volcanic conditions and lowly aquatic life, all peculiar to the planet in that far-off time, which are not to be understood in the present state of advancement of science. But it seems demonstrated that each forward step made by science unfolds to us more and more that nature works in simple rather than in complicated reactions; and catalysis, as experienced of late, must be regarded as an ever present, a powerful, and a simple phenomenon.

ACKNOWLEDGMENT.

The author finds pleasure in recording his acknowledgment to Mr. R. C. Allen, vice-president of Oglebay, Norton & Co., Cleveland, Ohio, and formerly State Geologist of Michigan, for the assistance which he gave so freely. His critical examination of the facts which form the basis for the author's views expressed in this paper, and the close scrutiny that he gave to the presentation made of those views, were very helpful.

MANAGER, IRON ORE PROPERTIES,
NORTHERN PACIFIC RAILWAY CO.,
BRAINERD, MINN.

THE SOLUBILITIES OF METALLIC SULPHIDES IN ALKALI SULPHIDE SOLUTIONS.

JOHN W. GRUNER.

INTRODUCTION.

THE problem of the solubility of metallic sulphides as sulphides in aqueous solutions has been discussed frequently. The solubilities, however, are far too small in water alone to be of geological importance. Aqueous solutions of sodium sulphide dissolve certain metallic sulphides easily and form double salts. The metals might possibly be transported in this form in the earth. Experiments by Becker,[1] Doelter,[2] Freeman [3] and others have frequently been cited in support of the belief that sulphides are carried as double sulphides. The only ones soluble in aqueous solutions of sodium sulphide are iron, gold, antimony and arsenic. They are said to be soluble in either cold or hot solutions. Mercury sulphide should also be included here, but no experiments were made with it by the writer.

Recently Fred Foreman [4] showed by experiments made in the writer's laboratory that under the conditions used, pyrrhotite and pyrite are not soluble in sodium sulphide solutions. These experiments were made in pyrex tubes at elevated temperatures.

Foreman's work was criticised recently by R. E. Stevens,[5] who found that pyrrhotite dissolves in sodium sulphide, forming dark green, probably colloidal solutions. Stevens [6] thinks that Foreman's solutions contained NaHS and not Na_2S, and criticises him

[1] Becker, G. F.: U. S. Geol. Survey, Mon. 13, p. 432, 1888.

[2] Doelter, C.: Mineral. pet. Mitt., vol. 11, pp. 321–324, 1889–90.

[3] Freeman, Horace: Eng. and Min. Jour., vol. 120, p. 973, 1925.

[4] Foreman, Fred: Hydrothermal Experiments on Solubility, Hydrolysis and Oxidation of Iron and Copper Sulphides. ECON. GEOL., vol. 24, p. 811, 1929.

[5] Stevens, R. E.: The Alteration of Pyrite to Pyrrhotite by Alkali Sulphide Solutions. ECON. GEOL., vol. 28, pp. 1–19, 1933.

[6] *Op. cit.*, p. 2.

for not explaining how these solutions were prepared and for using an atmosphere of CO_2 in "many" experiments. He also objects to Foreman's statements that the solutions "were alkaline or neutral in reaction." These criticisms are unfounded. In the first place, Foreman used Baker's sodium sulphide *crystals,* $Na_2S.9H_2O$ (p. 832 of his paper). This material was partially analyzed for the writer by Dr. T. Kameda. It will also produce green solutions if used in the manner in which Stevens used his solutions. Examination of Foreman's tables will show that he made more experiments with an atmosphere of nitrogen than with carbon dioxide. The statements as to the alkalinity of the solutions refer to the completed experiments and not, as Stevens thought, to the solutions before heating.

Stevens' high temperature experiments, made in platinum containers in steel bombs, although of great interest, are not as significant geologically as Foreman's, who made his in the presence of SiO_2 and in part in an atmosphere of CO_2. There is no doubt that SiO_2 would always be present under natural conditions.

ADDITIONAL EXPERIMENTS.

A number of experiments were made at 200° and 300° C. to determine the influence of SiO_2 on the solubilities of gold, iron, antimony and arsenic. The experiments at 200° C. were made in pyrex tubes (like Foreman's) from which the air was displaced by nitrogen. Those at 300° C. were made in silica tubes. The solutions were put into the silica tubes through narrow necks and the air displaced by nitrogen. Then the lower halves of the tubes were cooled to the freezing temperatures of the solutions. A vacuum pump was connected to the narrow outlets and after evacuation they were sealed with the hydrogen-oxygen torch. These silica tubes were enclosed in steel bombs which were partly filled with water to counteract the pressure inside the tubes. One gram of coarsely powdered mineral was used in each tube with approximately 25 cc. of solution. Each experiment lasted 24 hours. The solutions were prepared exactly as described by Stevens.[7]

[7] *Op. cit.*, p. 3.

Carbonate-free NaOH solution (0.509 N) was saturated with H_2S which had been passed through distilled water. H_2S was bubbled through for at least 1¾ hours in each experiment. Then an equal volume of NaOH was added.

Experiments with Pyrrhotite.—The pyrrhotite used was the purest obtainable from Sudbury, Ont. Polished fragments showed no inclusions of other sulphides. The material was crushed to a coarse powder just before use. When the Na_2S solution came in contact with it, it became greenish in color indicating slight temporary solution of iron sulphide. After the experiments, the solutions were white, and colorless, after filtering. Not a trace of iron could be detected except in one at 200° C. which contained possibly as much as one part of Fe per million. Much H_2S was liberated on opening the tubes, and large quantities of SiO_2 could be precipitated from the filtered solutions. Pyrex as well as silica tubes were badly decomposed. The reaction due to hydrolysis and attack of SiO_2 probably is:

$$2Na_2S + SiO_2 + HOH \rightarrow Na_2SiO_3 + 2NaHS.$$

The FeS does not seem to take part in the reaction at temperatures sufficiently high (200°–300° C.) to attack SiO_2 readily. Whether some FeS might possibly be converted to FeS_2 under these conditions could not be ascertained. The pyrrhotite after the experiments of 300° C. seemed to be covered with a film the color of pyrite, but microscopic examination of polished fragments showed no change. More time might be necessary for visible alteration to pyrite. To lengthen the time of the experiment, however, is not advisable on account of the rapid decomposition of the silica tubes.

Experiments with Gold.—Gold dissolves in Na_2S solutions to form double salts according to Becker,[8] Freeman[9] and others. Their experiments, however, were not made at high temperatures. Mr. S. Ogryzlo in connection with other experiments on gold, kindly made a number of experiments for the writer. Experiments at 200° C. in pyrex tubes on 24 carat sheet gold which

[8] *Op. cit.*
[9] *Op. cit.*

PARAGENESIS AS AN AID IN VALUING NEW DISCOVERIES.[1]

BOHUSLAV STOČES.

In many mining districts the order of deposition of the minerals in the several vein systems is definite and well known. The changes in the composition of the vein minerals from the walls inward may be due to one or more of several causes, such as changes in the composition or concentration of solutes of the mineral-bearing solutions emanating from the parent magma; a gradual lowering of the temperature; and change of pressure. Whatever the cause, the changes are apparently gradual and effective in all the fissures of any particular system.

If the order of deposition can be determined covering the whole period of mineralization, it may be of great assistance in judging the probable value of newly discovered veins in the district. The method of procedure will be apparent from a consideration of the following cases.

1. A *wide* fissure opened at the *beginning* of the period of mineralization would ordinarily receive deposits in a succession of bands through all the chemical and physical changes that take place in the magmatic solutions to the end of the period of deposition. The series would be complete and would include both valuable ores and worthless gangue.

2. A *narrow* fissure opened at the beginning would have deposited upon its walls the first mineral in the succession and would probably be completely filled by it. Such a fissure open from the beginning of mineralization would, therefore, contain valuable minerals only if such minerals were deposited in the first stage of mineralization. If, however, the first members of the mineral succession should be worthless, there would be small chance of finding valuable minerals on further exploitation.

[1] Presented before the Society of Economic Geologists, 13th Annual Meeting Princeton, N. J., July, 1933.

3. A *wide* fissure opened *during* the period of mineralization would, of course, receive on its walls whatever minerals were being precipitated at the time, and could be filled only with such minerals as follow in the established order. Whether or not such veins contain valuable deposits would depend, therefore, upon which members of the mineral succession follow before the fissure is filled.

4. A *narrow* fissure opened *during* the period of mineralization would also receive on its walls whatever minerals were being deposited at that stage and would probably be completely filled by that group alone. The mineral of the walls would, therefore, indicate the stage of opening of the fissure and also whether further exploitation is justified.

When the order of mineral succession has been established for a vein system, and especially when it has been determined at what stages the useful and the worthless minerals were deposited, a fair estimate can be made of the probable value of a newly discovered vein of the same system if it can be determined at which stage in the period of mineralization the fissure opened.

VYSOKÉ SKOLY BANSKÉ,
PRIBRAM, CZECHOSLOVAKIA.

DISCUSSION AND COMMUNICATIONS

*THE ORE DEPOSITS OF THE TRI-STATE DISTRICT.**

Sir: The paper of Fowler and Lyden[1] is a valuable contribution to economic geology presented wholly from the viewpoint of the mining geologist whose chief objective is to find all of the ore in a district at a minimum of development and mining cost. My personal contact with these men during a short visit to the district in 1927, after they had completed a study of a large portion of the Picher-Miami area, and my later conversations and discussions with both men, have convinced me that their conclusions on structure and shearing were not at all influenced by a desire to bolster up a preconceived notion that these areas were of igneous origin, as has been recently suggested by Dr. Leith.[2] I believe with them that these deposits are of igneous origin, but my personal examinations and studies in many of the mines did not confirm all that Fowler and Lyden have had to say about the structure and physical characteristics of the ore occurrences.

Their presentation of the geological history of these deposits is not clear with respect to the relation between the various processes of dolomitization, chertification, brecciation and later mineralization. For example, it is stated that "the dolomization, chertification and sulphide mineralization probably came from the same original source and were introduced into the Boone formation through the same general zones of adjustment." They

* Manuscript received before the publication of "The Miami-Picher Zinc-Lead District," by W. A. Tarr, in the August number of ECONOMIC GEOLOGY.—*Editor.*

[1] Fowler, G. M., and Lyden, J. P.: The Ore Deposits of the Tri-State District. Trans. Amer. Inst. Min. and Met., vol. 102, p. 206, 1932.

[2] Leith, C. K.: Structures of the Wisconsin and Tri-State Lead and Zinc Deposits. ECON. GEOL., vol. 27, pp. 414–415.

identify the early chertification and dolomitization with a deformation of pre-Cherokee age but associate the jasper and ore mineralization with an igneous activity certainly of post-Cherokee age. More recently Weidman [3] definitely places the chertification of the Boone as pre-Cherokee by identifying erosional Boone-chert pebbles in the Mayes, which is older than the Cherokee. Fowler and Lyden do not mention the existence of the Mayes formation. In view of this long-time interval between the period of early chertification and later sulphide mineralization, it seems logical to connect the early chertification with the orogenic disturbances responsible for the folding and crumpling of the Boone formation but having no connection with post-Cherokee igneous activity.

Fowler and Lyden lay much stress upon the rôle played by shattered zones, fissures, and shears as channelways through which the early chertifying solutions travelled, yet I was unable, during my examination of the Miami district, to find evidence to support that theory. The early chert shows no vertical arrangement along intersecting fissures or fissure zones. There is no replacement of wall rock along or adjacent to shears, cracks, or fissures such as is found in typical examples in other ore deposits where mineralizing solutions travel through fissures. On the other hand, the chert is strictly conformable to the bedding of the limestone. The occurrence of the early chert in the Picher-Miami area is typical of bedded cherts I have seen elsewhere, and these appear to be the result of obscure processes of metamorphism associated with regional deformation but not necessarily related to igneous activity.

The extent to which fissuring has determined the loci of ore deposits is an extremely difficult question to answer, for the reason that rock alteration with attendant slumping and brecciation in the Boone formation has largely obliterated the evidence of such early fissuring. During my visit to the Miami district I went through stope after stope in company with Fowler and Lyden,

[3] Weidman, Samuel: Miami-Picher Zinc-Lead District. Oklahoma Geol. Survey, Bull. 56. Univ. of Okla. Press, 1932.

with an open mind about shearing and fissuring, with the final result that I was far from being convinced that shearing had played the all-important rôle ascribed to it by these men. Only in rare instances did I observe fissures having recognizable continuity.

In this connection a reference to Plate III of Weidman's [4] work is of interest. This map purports to show the relation of shearing or fissuring to mined ore bodies. The conclusions which might be drawn are that there is no definite fracture pattern, and that there is no order of direction or course of the shears or fissures. Furthermore, as drawn, the fissures exhibit a remarkable parallelism and commonly they begin and end within the walls of the stope opening. Marked and sudden changes in strike are shown to be very common and the inevitable conclusion is that projections of fissures on strike made beyond the point of the pick into unexplored ground are wholly unreliable and most hazardous. Study of Plate III prompts the question whether the stopes were following a series of shear planes, or the shears were drawn to fit the stopes.

Just as there is no vertical arrangement of chertification along so-called fissures or shears, similarly there are no jasper, sulphides, or any vein minerals whatsoever, arranged crosswise of the bedding along steep dipping shears cutting the Boone. The argument that such shearing or planes of readjustment as may now be recognized within the lateral limits of the ore bodies were important as channelways for solutions depositing ore becomes to some degree, at least, a supposition receiving but little support from facts disclosed in mine openings.

It may be assumed, I think, that some fissuring or shearing accompanied the first crumpling and folding of the Boone. According to Fowler and Lyden (Fig. 14) the Miami fissure zone is pre-Cherokee, therefore older than the igneous activity responsible for the introduction of the ores. Whether the post-Cherokee igneous activity resulted in new fissuring being imposed upon that already in existence, is also a question difficult of solution.

[4] *Idem*, p. 40.

It is well to note that there has been little or no faulting or fissuring since sulphide deposition ceased.

It seems certain that subsequent to the extensive early chertification of the Boone, but prior to the advent of the jasper and sulphide mineralization, the Boone formation in this area suffered marked physical change and alteration resulting in wholesale settling, slumping and collapse involving that part of the Boone in which the ore bodies occur. Where solution activity was most intense, important thicknesses of the Boone were involved, resulting in jumbled breccia areas or pipes composed of chert, dolomite, limestone, etc., cutting vertically through that formation, in places reaching and involving the overlying Cherokee. The chert suffered no chemical change; the collapse was therefore due to marked shrinkage and loss of compressive strength within certain unchertified layers of Boone. Every gradation may be noted, from incipient brecciation due to the superincumbent gravity load acting upon alternate layers of chert and weakened limestone, to the more extensive collapse-breccias just noted. An excellent example of gravity load brecciation is exhibited by the bottom six feet of "M" bed, one of the most persistent ore horizons of the district. In this bed there may be seen every gradation, from a less disturbed unmineralized condition where it is composed of alternate bands of dark gray to black, soft, weak, almost powdery material, and hard, white, unbroken chert, through successive stages of collapse and brecciation where it becomes a mixed-up jumble of shale and angular, sharp-edged chert fragments. Subsequent introduction of mineralizing solutions has added silica and sulphides to form the two- to four-foot band of hard, dark brown or black jasperoid ore-breccia so commonly seen in stope faces at or near the bottom of the ore column.

This intermediate period of alteration of the Boone must be recognized as a very important one as far as the Picher-Miami area is concerned. The early condition of the Boone, whatever it was as to fissuring, shattering or shearing, was later profoundly modified before mineralization began. The porosities of certain of the Boone strata were enormously increased, and this rock

condition, together with collapsed and slumped areas, and brecciation, afforded an unusual and remarkably favorable condition for rock penetration by mineralizing solutions. Such fissures or shears as may have existed at the close of the early deformation period were largely obliterated and thereafter played a minor part as channelways in the Boone for solutions depositing jasper and sulphide minerals. The general absence of mineral deposition in or along shear cracks or fissures is convincing evidence on this point.

The uprising mineralizing solutions, having once gained access to the productive horizons of the Boone, moved laterally freely through these zones of intense alteration and brecciation. It is not necessary to look to local shearing as the channelways through which ore solutions from below ascended to reach the individual ore runs where sulphides were deposited. A single fissure zone such as the Miami extending downward from the brecciated Boone to sources of mineralization below, would be sufficient to supply the sulphides of this entire area, because of the slight resistance to lateral travel in the ore horizons. It is well to note here that there is actual ore continuity between nearly all the important mines of the Miami-Picher district.[5]

The history of these deposits is probably not essentially different from the cycle exhibited by many other ore deposits of Western United States where the deposition of ore was preceded by solutions or gases profoundly altering the rocks which were later to receive the sulphide ore minerals. The early, rather gentle folding in the Picher-Miami area was no doubt accompanied by some cracking, fissuring, or shearing of the Boone and the underlying Ordovician dolomites. These underlying dolomites might well be considered as the source of the dolomite now found in the ore horizon, the transportation of the dolomite from the underlying Ordovician to the Boone having been effected by mineralizing solutions originating at greater depths.

I find myself puzzled over the following statement made by the authors relating to the transportation of Cherokee shale.[6]

[5] Fowler and Lyden: *Op. cit.*, Fig. 5.

[6] *Idem*, p. 14.

Shale, which was deposited during Cherokee times, is now often found in the disturbed areas of the Boone formation in openings of all sizes and shapes and in places sometimes 300 feet or more below the top of the Boone. In some areas it travelled laterally for long distances from the contiguous shear zones in the Boone formation, through which it was transported downward into the ore-bearing horizons. Shale precluded the deposition of ore, particularly zinc, in some zones which were otherwise favorable.

Mr. Fowler, in oral discussion with the writer, has elaborated upon that statement. It will be recalled by those familiar with the ore bodies of the Picher-Miami area, that the lower six feet of the so-called "M" bed, where not soaked up with silica to form jasperoid, is black or nearly so, closely resembling highly carbonaceous shale. The six-foot bed also discloses within it, where not brecciated, three or four layers of clean white chert. Although it is not clear from the quoted statement above that the authors have in mind the black shaly material in the six-foot bed just described, Mr. Fowler states definitely that it is his belief that the dark gray to sooty black coloring in the six-foot bed results from the transportation of Cherokee shale from above, presumably through the medium of downward-moving surface waters.

It is inconceivable that water could have caused a substantial lateral migration of shale. I can well understand surface waters picking up finely divided particles of shale resulting from surface decomposition and carrying them downward through open cracks or very open porous breccias, to deeper rocks, where the fine material in suspension would probably be deposited as mud or silt. I have seen in other districts local accumulations of mud and sand or silt in open fractures or cavities in limestones many hundreds of feet underground, but mud accumulations are not necessarily of surface origin. In all my trips underground in the Picher-Miami district I saw but little to indicate that circulating waters had transported substantial quantities of shale to the ore zone, and I wholly disagree with Fowler's verbally stated belief that the dark color of certain bands of bed "M" are related to the Cherokee. And, in view of the statement by the authors

quoted above that "shale precluded the deposition of ore, particularly zinc, in some zones which were otherwise favorable," it is interesting to note that the dark six-foot band of "M" bed above discussed is the most persistently mineralized and highly productive bed in the entire district. That the black coloring was pre-mineral in age is proved by the gray to black color of the so-called jasperoid.

RENO H. SALES.

BUTTE, MONT.

REVIEWS

History of the Theory of Ore Deposits, with a Chapter on The Rise of Petrology. By THOMAS CROOK. Pp. 163. Thos. Murby & Co., London, 1933. Price, 10s. 6d.

This very readable account of the history of the development of the various theories that have been proposed to explain the origin of ore deposits, outlines in clear strokes the controversy that has existed for nearly two hundred years over the manner of formation of veins and other ore deposits. "A striking feature of this history," writes the author, "is the way in which the fashion of theorizing . . . seems to have run in cycles. A remarkable example of this is the repeated resurrection of the ore-magma theory, which has been revived in recent years Introduced by Hutton in the eighteenth century, again by Fournet in the first half of the nineteenth and yet again by Belt in the second half of the nineteenth, it has, during the present century, found its most thorough-going exponent in J. E. Spurr."

The last chapter gives a very brief survey of the development of petrology with the purpose, perhaps, of showing that the earlier students of the subject had a wider and more practical outlook than that of most modern petrologists, in that the former "sought to establish a common basis of theory and classification for rocks and ore deposits."

The author's thesis, which is intimately interwoven with the history, is that "the foundation of the study of ore deposits, like that of rocks, is geodynamical; and, that the study of ore deposits is as genuine a part of the science of petrology as is the study" of rocks. The earlier petrologists like Haüy and Cordier realized this, but later ones allowed their science "to degenerate for all practical purposes into a study of silicate rock masses . . . whereas it should have been applied to mineral deposits generally. . . . With its present restricted scope, petrology has no claim to recognition as a definite science." The author appears to have overlooked entirely the contributions that men trained in petrographic methods have made to the study of ore deposits through the application of these methods to polished sections of ores.

The author's bias in favor of the Neptunistic theory of ore deposits is shown in his statement that most "of the value of the world's total annual

output of minerals at the present time is from concentrations in the outer crust that can safely be attributed to . . . sedimentary and metamorphic agencies, in which meteoric water has played an overwhelmingly predominant part. We may therefore reasonably infer that the modern igneous theory of metalliferous veins is not in harmony with the main facts to be accounted for. . . . Indeed a little hard thinking on the facts already known will . . . do something to secure for exogene agencies the recognition due to them as the chief agencies by which metalliferous and other minerals have been concentrated in the outer crust of the earth." And in his concluding remarks at the close of his historical outline he states that in the future "it is reasonable to expect that there will be a growing recognition of the inadequacy of igneous magmas as direct and self-sufficing sources of supply of metalliferous and other material for lode formation." On page 32, after referring to the vague notions of the geologists of the later part of the 18th century, with respect to the origin of ore veins, he remarks that "however much we may be inclined to regard these early speculations as lacking in scientific foundation, we may reasonably doubt whether, in this respect, they were, after all, very far inferior to the dominant speculations entertained on this subject at the present day."

In spite of the point of view from which the author handles the opinions of past students of ore deposits, his "History" is an interesting and worthwhile book. It gives an excellent outline of the development of the theories concerning the origin of ore bodies, and at the same time, because of its strong prejudice in favor of meteoric water as the dominant agent responsible for ore concentration, it should serve as a tonic to those who prefer to explain most ore bodies rather as the result of agencies initiated by magmas. It should lead them to test their own theories in order to discover whether they are well established in fact or not. The book is well written and well printed. A very valuable feature is the inclusion in the text of many significant quotations from the writings of those who are cited as having made important contributions to the subject discussed.

W. S. BAYLEY.

The Economics of Mining. By T. J. HOOVER. Pp. 547, figs. 11. Stanford Univ. Press, Calif., 1933. Price, $6.00.

This comprehensive volume is divided into three parts. Part I, Mine Valuation, deals with sampling, extension of ore deposits (geology), ore reserves, financing, and marketing. Part II, Mine Organization, deals with the organization, promotion, mining investment, valuation of shares,

and law. Part III, Mine Management, takes up the various problems that confront the mine manager. Each subject is concluded with an excellent bibliography. The subjects are treated comprehensively and it forms a valuable reference.

On The Mineralogy of Sedimentary Rocks. By P. G. H. Boswell. Pp. x + 393. Thos. Murby & Co., London, 1933. Price, 21s. and duty.

Professor Boswell in his new book has given us an account of the progress made in the study of sedimentary rocks through the aid of heavy minerals. It contains practically all the information on the subject available in published articles prior to the establishment of the "Journal of Sedimentary Petrology" by The Society of Economic Paleontologists and Mineralogists, and thus, together with this journal, gives a continuous summary of the work on heavy minerals in sedimentary rocks from the beginning to the present time.

The book is divided into three parts. Its first part is a running comment on the significant contributions dealing with the subject treated historically under various heads, such as the stability of detrital minerals: clues to the sources of sediments; correlation by heavy minerals; characteristics of shore sands, of dune sands, and of deep-sea deposits; authigenic minerals and the mineral composition of clays. Under each heading are collected the significant results that have appeared in the publications of various workers so far as they apply to the feature discussed. The results are summarized and their applications are emphasized.

Its second part comprises a list of 1025 publications, each of which is briefly abstracted in such a way as to give a rather thorough idea of its contents. This is particularly valuable, for, "since many of the publications . . . are difficult of access, the addition of the abstracts may save other investigators much of the trouble that had to be taken in the first instance and should obviate the waste of time in fruitful research."

The third part consists of a general index to the contents of the book and special indices to stratigraphical horizons, localities, minerals, figures of minerals, and technique referred to in the various publications abstracted. This part will prove to be of immense value to all students who desire to go into the study of sediments in any great detail.

The volume, as will be noted from the outline given, is not a text-book, nor primarily a history, but is rather a compendium of knowledge concerning the character of heavy minerals in sedimentary rocks and of the conclusions that have resulted from their study.

W. S. Bayley.

Mineral Deposits of the Canadian Shield. By E. L. BRUCE. Pp. xxiv + 428, figs. 161. Macmillan Co. of Canada, Toronto, 1933.

This book is designed to fill the need for information concerning the mineral deposits of the Canadian Shield that has arisen because of their rapid development during the past few years. The first 105 pages contain a general and somewhat elementary treatment of some of the principles of geology and ore deposition. The remainder is descriptive of the geology, both local and in its regional relationship, of several dozen selected mines. The author is to be congratulated on the fine organization and presentation of the material, the abundance of footnote references to original sources, and the number and excellence of the illustrations.

BOOKS RECEIVED

BY

DAVID GALLAGHER.

Potash. By B. L. JOHNSON. Pp. 78, 1 fig. U. S. Bureau of Mines, Economic Paper 16. Washington, 1933. 10 cents. Occurrence, uses, technology, and world potassium situation.

Cement in 1931. By B. W. BAGLEY. Pp. 29. U. S. Bureau of Mines, Mineral Resources, 1931—Pt. 2. Washington, 1933. 5 cents. Production statistics.

Crude Petroleum and Petrolem (sic) Products in 1931. By G. R. HOPKINS AND A. B. COONS. Pp 122, figs. 16. U. S. Bureau of Mines, Mineral Resources, 1931—Pt. II. Washington, 1933. 10 cents. Production statistics.

Mineral Resources of the United States, 1930. Part I—Metals. By O. E. KIESSLING ET AL. Pp. 1142. U. S. Bureau of Mines. Washington, 1933. Price, $1.50.

The Mineral Industry during 1932. Vol. 41. By G. A. ROUSH. Pp. 680. McGraw-Hill Book Co., Inc. New York and London, 1933. Price, $12.00. The well known annual volume on mineral statistics, technology and trade.

Illinois Mineral Industry in 1932. By W. H. VOSKUIL AND A. R. SWEENY. Pp. 66, tables 45. Illinois Geol. Surv., Rept. of Inves. No. 28. Urbana, 1933.

Geology and Mineral Deposits of Southern Yuma County, Arizona. By E. D. WILSON. Pp. 236, pls. 29, figs. 7. Ariz. Bureau Mines, Geol. Series 7, Bull. 134. Tucson, 1933. Regional geology and descriptions of the individual mines and claims.

SCIENTIFIC NOTES AND NEWS

Glenn C. Bartle is professor of geology and head of the Division of Physical Sciences in the recently organized University of Kansas, at Kansas City, Missouri.

George C. Martin, of Washington, D. C., is spending the winter with his son at 503 N. 13th Street, Corvallis, Oregon, where he is available for consulting work.

Richard W. Smith, assistant State geologist of Georgia, is now acting State geologist on account of the death of S. W. McCallie.

W. L. Whitehead, of the Massachusetts Institute of Technology, has been examining properties in the Mother Lode gold mining district of California.

John B. Stone, geologist for Colorado Fuel and Iron Company, Pueblo, Colorado, has resigned his position to take up professional work in Australia. His address will be: Metals Investigation Proprietary, Ltd., Collins House, 360 Collins Street, Melbourne C–1.

W. H. Collins, director of the Canada Geological Survey, delivered at Northwestern University on November 21 to 23 a series of lectures on: The Economic Future of Northern Canada, Major Correlational Problems of the Great Lakes Region, and The Sudbury Mining Field. This inaugurates a series made possible by a fund created by friends of the late Professor U. S. Grant to commemorate his services as scientist and teacher.

Philip S. Smith, chief Alaskan geologist of the U. S. Geological Survey, has been appointed by Administrator Ickes as representative for Alaska of the Federal Emergency Administration of Public Works, with headquarters at Juneau.

The Geological Society of Chicago was addressed on November 23d by W. H. Collins, of the Canada Geological Survey, on "The Behavior of Some Basic Magmas."

The Society of Economic Geologists will hold its annual meeting at Chicago, December 28 to 30, in conjunction with the Geological Society of America and under the auspices of the University of Chicago and Northwestern University. Registration will be at the Reynolds Club, and technical sessions at the University of Chicago. The presidential address by Edson S. Bastin will be delivered on December 28, at 3:00 P.M., on The Primary Native Silver Ores, and the annual business meeting will be held immediately following it. Visitors are welcome.

Samuel W. McCallie, state geologist of Georgia, died suddenly on October 26, after having served the State for forty years, as assistant geologist from 1893 to 1908, and state geologist from 1908 until his death.

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